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ON THE SYNTHESIS OF HELICIN AND PHENOL-GLUCOSIDE.

By ARTHUR MICHAEL.

In 1837, while examining amygdalin, Woehler and Liebig* investigated its behavior towards an aqueous solution of emulsin, and found that it decomposed under the formation of grape sugar, benzoic aldehyde and hydrocyanic acid. This is the first instance in which a carbohydrate was known to enter into the composition of an organic body. A short time later, Piria† with salicin, and Stas‡ with phloridzin, demonstrated that these compounds are decomposed by dilute acids, under the formation of grape sugar among other products. Since that time, hardly any class of compounds has been found more numerous, and more widely spread, in organic nature than similar bodies, which are now classed under the generic name of the glucosides.

The glucosides are usually considered as mixed ethers of glucose and their other respective constituents; an hypothesis which explains, in some measure, the simplicity of their products of decomposition. It will be found, however, that many of them present properties which are not strictly in accordance with this hypothesis. I may mention the great stability of most of the glucosides towards easily reducible metallic salts; a property which certainly would not lead us to presuppose the presence of the aldehyde group of glucose, and which, according to the above mentioned hypothesis, exists in the glucosides unchanged. Again, their remarkable behavior towards dilute acids, and certain ferments, is not in accordance with the properties of any compound known to belong to the ether group.

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*Ann. Chem. Pharm. 22, 1. †Ibid. 30, 151. ‡Ann. de Chemie et Phys. 69, 367.

P. Schuetzenberger* was the first to publish experiments on the synthesis of the glucosides. He allowed di- and triacetoglucose to act on the sodium† and lead salts of saligenin and rhamnetin, but he only obtained baldly-defined compounds, which appear to have contained glucose as one of their constituents; however, neither the analyses nor the properties of these compounds corresponded with those of the natural glucosides. I have undertaken the synthesis of the glucosides in a different manner; starting from the interesting compound discovered by A. Colley‡ while examining the action of acetylchloride on glucose, and known under the name of acetochlorhydrose. This compound, which presents the rational formula $C_5H_6Cl(OC_2H_3O)4CHO$, I have allowed to act on potassium phenate and potassium salicylite, and have obtained compounds which possess all the characteristic properties of the glucosides.

In the preparation of acetochlorhydrose, I have little to add to the excellent directions given by Colley in his memoir; but will call attention to the fact that a finely powdered glucose is absolutely necessary, and that when 10 gr. of glucose are employed the reaction is not finished in less than 48 hours.

Action of Acetochlorhydrose on an Alcoholic Solution of Potassium Phenate.

After numerous experiments, I found the following conditions to yield the most satisfactory results: 27.5 gr. of acetochlorhydrose were mixed with about twice its volume of absolute alcohol, and the solution added to a cold alcoholic solution of 10 gr. of potassium phenate. After a few minutes, a crystalline precipitate began to separate from the solution, and at the same time a strong odor of acetic ether was noticed. The reaction proceeded very rapidly, and after four or five hours no further separation of the crystalline substance was observed. The solution was then filtered, and the precipitate examined, which proved to consist of potassium chloride, mixed with a small quantity of amorphous organic matter. The filtrate from the potassium chloride was allowed to evaporate in a flat basin by exposure to the air, and left an oily substance, which, after standing several hours, solidified to clusters of concentrically grouped needles. These crystals were then well pressed between bibulous paper, to free them from an oily substance which would, if left, render their purification very difficult, and they were then easily obtained in a pure state by treating with animal charcoal and crystallizing twice from water.

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*Compt. rend. 69, 350.

†This salt was not analyzed, and after the experiments of Beilstein and Seelheim (Ann. Chem. Pharm. 117, 89), it is doubtful whether it is a derivative of saligenin.

‡Compt. rend. 70, 401.

The substance crystallizes from a hot aqueous solution in long, concentrically grouped, odorless, white needles, which melt at 171-172°, and solidify on cooling. It is moderately soluble in cold, and very soluble in warm water. Alcohol and acetic acid dissolve it quite readily in the cold. The aqueous solution has a very bitter taste, and turns the plane of a polarized ray of light to the right.

The most interesting property of this substance is its behavior towards dilute acids and emulsin. A dilute solution of sulphuric or chlorhydric acid decomposes it on gently warming very readily in glucose and phenol: warmed for a short time with an aqueous solution of emulsin the same decomposition is effected. The formation of phenol and glucose was proven by their isolation, and by all their characteristic reactions, and they are the only products of the decomposition; especially, the presence of acetic acid could not be detected. A warm, dilute solution of potassium hydrate decomposes it in a like manner. Concentrated sulphuric acid dissolves it in the cold without decomposition with a yellow color; on the addition of water to this solution, the above mentioned decomposition was observed. An analysis of the compound, dried at 100°, gave: .2112 gr. of substance gave .4385 gr. of CO_2 and .1207 grms. of H_2O.

		Calculated for $C_{12}H_{16}O_6$.	Found.
C	...	56.25	56.62
H	...	6.25	6.35
O	...	37.50	37.03

The results of the proximate analysis, and the products of its decomposition, leave no doubt as to the nature of this compound. It is a mixed ether of phenol and glucose, and as its properties correspond entirely with those of the glucosides, although it has never been observed in organic nature, it may be called phenolglucoside.

The constitution of phenolglucoside is expressed by the formula $C_5H_6(OC_6H_5)(OH)_4CHO$, and its formation is according to the following equation:

$$C_5H_6Cl(OC_2H_3O)_4CHO + C_6H_5OK + 4\,C_2H_5OH =$$
$$C_6H_5(OC_6H_5)(OH)_4CHO + KCl + 4CH_3COOC_2H_5.$$

This reaction consists of two parts; one of which, the substitution of the acetyl groups by the hydrogen of the alcohol,* was not foreseen, although the formation of acetic ether by heating alcohol with tetra-acetohelicin, a fact which was observed by H. Schiff,† several years ago, indicates a similar decomposition of that compound. The facility with which the alcohol acts in this reaction is owing to the fact that the sum of the negative forces acting on each of the oxygen atoms which connect the acetyl groups with the glucose rest, exceeds the negative power of the radical $C_2H_5O^I$, and the positive hydrogen atoms of the alcohol, therefore substitutes the negative acetyl groups.

Action of Acetochlorhydrose on an Alcoholic Solution of Potassium Salicylite.

The properties of phenolglucoside indicate that this compound belongs to the group of natural glucosides, and made it probable that the glucosides obtained by synthesis would not prove isomeric, but identical with those occurring in nature. I have first undertaken the synthesis of helicin, by allowing acetochlorhydrose to act on potassium salicylite.

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*The action of absolute alcohol on the compounds obtained by dehydrating with acetic anhydride, as hexacetatediglucose, presents considerable interest. I shall also return, in a future paper, to the action of acetylchloride on lævulose, and other carbohydrates.

†Ann. Chem. Pharm. 154, 23.

The latter compound was made by adding 1 mol. of salicylic aldehyde to 1 mol. of potassium hydrate dissolved in absolute alcohol, and afterwards adding an equal volume of ether, which caused a further precipitation of the potassium salt. This salt is but moderately soluble in absolute alcohol, 1 part requiring about 20 parts of it.

The action of acetochlorhydrose on this salt was studied under conditions similar to those employed in the synthesis of phenolglucoside. Equivalent quantities of the two substances both dissolved in absolute alcohol, were allowed to react in the cold, and the action was accompanied by the separation of potassium chloride and formation of acetic ether; it proceeded, however, very slowly, and I found it advisable to allow the solution to stand three days before filtering from the potassium chloride. The filtrate was then evaporated by exposure to the air in an open vessel, and left a dark, oily residue, which, after standing ten days, partially solidified. It was well pressed between bibulous paper, and, after repeated treatment with animal charcoal, crystallized three times from warm water.

An analysis of the substance, dried at 100°, gave results which correspond well with the formula $C_{13}H_{16}O_7$. .2100 gr. of substance gave .4206 gr. of CO_2 and .1124 gr. of H_2O.

		Calculated.	Found.
C	...	54.93	55.09
H	...	5.63	5.90
O	...	39.44	39.11

The compound, therefore, has the empirical formula of helicin, and a comparison of the following properties with those of that glucoside, will show that the two bodies are identical.

When deposited from hot water, it crystallizes in small, white, odorless needles, which contain water of crystallization, and have a bitter taste. It is but sparingly soluble in cold and very readily in warm water; in warm alcohol it is also very soluble, but is insoluble in ether. The crystals melt at 175-176° to an olive-colored liquid, which solidifies on cooling: when heated for some time above its melting point, it decomposes with the evolution of salicylic aldehyde, and forms a liquid which solidifies finally to a yellow resinous mass. The aqueous solution does not reduce silver nitrate or ferric chloride, even on boiling, and is not precipitated by a solution of mercuric chloride or lead acetate. It is easily decomposed by boiling with very dilute sulphuric or chlorhydric acid into glucose and salicylic aldehyde (the presence of acetic acid could not be detected); and under the influence of an aqueous solution of emulsin, when heated at 30°, it undergoes a like decomposition. Dilute alkaline solutions dissolve it in the cold more easily than water, but without change; on boiling this solution it is decomposed as above. A solution of potassio-tartrate of copper does not decompose it in the cold, or even when heated at 50°, but after boiling this solution for several minutes a gradual reduction takes place, doubtlessly owing to the previous formation of glucose. Concentrated sulphuric acid dissolves it in the cold, the solution taking a chrome-yellow color. A drop of this solution placed on a strip of zinc foil, and approached by a drop of distilled water takes a red coloration at the point of contact, owing to the formation of salicin[*]. Since helicin has been reduced to salicin[†], its synthesis is therefore identical with that of the latter compound. The constitution of helicin or ortho-formylphenol-glucoside, is, therefore, $C_5H_6(OC_6H_4CHO)(OH)_4CHO$, and its formation by synthesis is expressed by the following equation:

$$C_5H_6Cl(OC_2H_3O)_4CHO + C_6H_4OKCHO + 4C_2H_5OH = C_5H_6(OC_6H_4CHO)(OH)_4CHO + KCl + 4CH_3COOC_2H_5.$$

The synthesis of helicin according to the above described reaction, does not show which of the hydroxyl groups of glucose is the means of connecting the glucose- and salicylic aldehyde-rests; but I may mention here that an investigation of the products which may be obtained by the double decomposition of acetochlorhydrose with numerous reagents, will undoubtedly give a clue to the solution of this problem. Acetochlorhydrose possesses a power of reaction which is only surpassed by that of the acid chlorides; a property which is doubtlessly due to the strong negative character of the body. A better example of its substituting power could hardly be given than the described reactions, which are the first instances of a paraffin chloride substituting directly the base of an aromatic phenate in the cold.

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[*] H. Schiff, Ann. Chem. Pharm. 154, 26. The action of nascent hydrogen on synthetical helicin will be studied later more fully, also its and natural helicin's behavior towards a ray of polarized light.

[†] Lisenko, Zeitschr. Chem. 1864, 577.

I have made several preliminary experiments on the substitution of the chlorine atom of acetochlorhydrose, and which indicate that this compound will permit similar substitution of the glucose radical—$C_7H_6O(OH)_4$—as the monohaloid derivatives of the paraffins permit with the paraffin radicals. It yields with ammonia, sodium ethylate and sodium aceto-acetic ether defined compounds, and acts on an alcoholic solution of potassium lævulosate with the formation of acetic ether and the separation of potassium chloride; on lævulose itself at 100° with evolution of chlorhydric and acetic acids, forming a small quantity of a new crystalline compound, possibly dextro-lævulose* or cane sugar.

I called attention in the beginning of this paper to the stability of many of the glucosides towards easily reducible metallic salts; this is the case with helicin, which has just been shown to contain the aldehyde group of glucose unchanged. I do not think that at present any satisfactory explanation can be given for this anomaly, and it therefore remains a fact which is not in accordance with the rational formula of the compound. On the other hand, the ease with which helicin is decomposed by acids will be understood when we consider the facility with which acetochlorhydrose substitutes its chlorine atom; it is owing to the same reason, the negative character of the glucose radical which enters into the composition of the glucoside.

Action of Acetochlorhydrose on an Alcoholic Solution of Sodium Saligenin.

The action of metallic sodium on a solution of saligenin in ether yields, according to the experiments of Beilstein and Seelheim,† a sodium derivative of saliretin, and the results I have obtained by the action of acetochlorhydrose on the compound tend to confirm their view.

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* The proof that helicin is an ether of glucose and salicylic aldehyde, notwithstanding its stability towards metallic salts, strengthens the hypothesis of cane-sugar being a mixed ether of glucose and lævulose; since the principal objection against this view is in the much greater stability of cane sugar than glucose towards easily reducible salts, whereas a natural supposition would have given it a greater reducing power, since it contains two aldehyde groups.

†Ann. Chem. Pharm. 117, 89.

Acetochlorhydrose acts on an alcoholic solution of sodium saliretin very readily, forming acetic ether and potassium chloride. The filtrate left on evaporation an oily substance, which solidified to a yellow, gelatinous, bitter mass, soluble in cold water, and which is very probably the glucoside of saliretin, since it is decomposed by dilute sulphuric acid or emulsin in glucose and saliretin.

The above described reaction will probably permit the synthesis of many of the glucosides, and promises to be of considerable interest in those cases in which doubt exists as to the constitution of these compounds, as, for instance, is the case with arbutin. I shall return to this subject in some future paper.

BUFFALO, N. Y., *Oct.* 11, 1879.

ON A NEW FORMATION OF STILBENE AND SOME OF ITS DERIVATIVES.

BY ARTHUR MICHAEL.

The following investigation was made above a year ago, and I had hoped to be able to complete it in a more satisfactory manner, but as there is little probability that I shall in some time be able to return to this subject, I intend to give a short description of the results I obtained, notwithstanding their incompleteness.

W. H. Perkin found, several years since, that by the action of anhydrous sodium acetate on a mixture of benzoic aldehyde and acetic anhydride, the synthesis of cinnamic acid could easily be effected, and generalized this reaction by taking not only different aromatic aldehydes, but also various fatty acid anhydrides. The action of sodium acetate on a mixture of phthalic and acetic anhydrides gives, as Gabriel and myself have shown, a remarkable acid, which we have called phthalylacetic acid;* subsequently, we found that the same reagent when used to dehydrate mixtures of phthalic anhydride and organic acids, instead of their anhydrides, always gave ketones;† this was shown to be the case with phenylacetic, succinic and isobutyric acids, and the reaction is doubtlessly much more general. It seemed to me to be of considerable interest to examine the action of dehydrating agents on mixtures of aromatic aldehydes and organic acids, which should give, were the reaction similar to that of phthalic anhydride and acids, unsaturated hydrocarbons, instead of unsaturated acids obtained by the reaction of Perkin.

I first examined the action of sodium acetate on a mixture of benzoic aldehyde and phenylacetic acid, and have obtained stilbene, in this manner, in large quantities. For this purpose, equivalent quantities of benzoic aldehyde, phenylacetic acid and anhydrous sodium acetate, were heated to boiling in an open flask, connected with a condenser, but I found that under these conditions no action ensued. The same mixture was next heated in a closed tube for about 12 hours at 250°, and upon opening the tube it was found to contain a considerable quantity of carbonic acid. The contents of the tube were extracted with boiling water, subsequently with warm dilute ammonia, to remove traces of unchanged phenylacetic acid, and the insoluble residue, which melted under warm water, was treated with animal charcoal, and finally crystallized several times from warm alcohol. The substance, dried at 100°, was analyzed with the following results: .2105 gr. of substance gave .7187 gr. of CO_2, and .1309 gr. of H_2O.

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* Deutsch. ch. Ges. Ber. 1877, 391. The rational formula of phthalylacetic acid, $C_6H_4\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}CH-COOH$, was based, not only on the properties of this compound, but also on the analogy it thus presented to the phthaleins of Baeyer. Lately, Baeyer has shown that the phthaleins are derivatives of triphenylmethane, and, therefore, by the dehydration that it is the carbonyl-oxygen atom ($C=O$), and not the anhydride oxygen atom $\left(\begin{smallmatrix}C\\C\end{smallmatrix}{>}O\right)$ which enters into the formation of the eliminated molecule of water. This brings the formula of phthalylacetic acid again into question, which would have the rational formula, $C_6H_4\begin{smallmatrix}C\\CO\end{smallmatrix}{>}O=CH-COOH$, were the reaction in this case similar to that of the phthaleins. This new formula explains the behavior of the acid towards bases very satisfactorily, but the dibasic acid formed, $C_6H_4\begin{smallmatrix}C(OH)=CH-COOH,\\COOH\end{smallmatrix}$ ought to possess properties, which would not be in accordance with those of the acid obtained. Not only are we at a loss to understand its remarkable instability towards heat and bases, but the compound obtained by the action of bromine upon it, which would have the rational formula, $C_6H_4\begin{smallmatrix}C(OH)Br-\\COOH\end{smallmatrix}$ $CHBr_2$, yields, when decomposed by bases, bromoform and phthalic acid, whereas, according to the new rational formula, methylene bromide, phthalic and hydrobromic acid should have been obtained. There are other decompositions of phthalylacetic acid which would not be satisfactorily explained by the new formula, and it is, therefore, advisable to accept for the present the formula as originally proposed.

† Deutsch. ch. Ges. Ber. 1877, 1559, 2207; 1878, 1007, 1679.

		Calculated for $C_{14}H_{12}$.	Found.
C	...	93.33	93.12
H	...	6.67	6.91

The compound, therefore, possesses the empirical formula of stilbene, and I found by a comparison of their properties, that they coincided with each other in every respect. The yield of stilbene according to this new method, is very satisfactory; I should judge from 50 to 60 per cent. of the theoretical, and the method may therefore be recommended for the preparation of this substance.

The formation of stilbene by the action of benzoic aldehyde on phenylacetic acid, is expressed by the following equation: $C_6H_5CHO + C_6H_5 - CH_2 - COOH = C_6H_5 - CH = CH - C_6H_5 + CO_2 + H_2O$.

The above described reaction is not only a convenient method for the preparation of stilbene, but firstly, by varying the aromatic aldehyde; secondly, by taking substituted derivatives of phenylacetic acid; and thirdly, by taking substituted derivatives of both the aldehyde and acid, numerous substitution derivatives of stilbene in the benzene nucleus may be obtained; and it is, therefore, of considerable interest, since the usual methods of obtaining substitution products of aromatic hydrocarbons in the benzene nucleus are, to a great extent, unavailable for the preparation of stilbene derivatives.

I have hitherto only examined the action of sodium acetate on mixtures of cumic and salicylic aldehydes with phenylacetic acid, and have obtained results in accordance with those anticipated. Equal parts of cumic aldehyde and phenylacetic acid were well mixed with about one-third part of anhydrous sodium acetate, and the mixture heated in a closed glass tube for about 15 hours at 250°. Upon opening the tube it was found to contain a considerable quantity of carbonic acid, and its contents were extracted several times with warm water, then with dilute ammonia, and left a residue, which melted under warm water. This residue was treated, in alcoholic solution, repeatedly with animal charcoal, and finally crystallized three times from a hot solution of the same solvent.

The substance thus obtained crystallizes in fine, glittering scales, which congregate in clusters that resemble cauliflower in their form. It is insoluble in cold and very slightly in warm water. In cold alcohol moderately, but very soluble in warm. It melts at 83–84°, and solidifies on cooling. The compound acts towards bromine as an unsaturated body, absorbing that reagent and forming a bromine additional product, which was not examined.

The substance, dried in vacuum, was analyzed: .1845 gr. of substance gave .6186 gr. of CO_2 and .1416 gr. of H_2O.

		Calculated for $C_{17}H_{18}$.	Found.
C	...	91.89	91.47
H	...	8.11	8.53

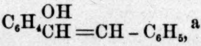
The empirical formula $C_{17}H_{18}$ is expressed rationally by $C_6H_4{}^{C_3H_7}_{CH} = CH - C_6H_5$, and the compound may therefore be called isopropylstilbene, its formation being according to the following equation: $C_6H_4{}^{C_3H_7}_{CHO} + C_6H_5 - CH_2COOH =$ $C_6H_4{}^{C_3H_7}_{CH} = CH - C_6H_5 + CO_2 + H_2O$.

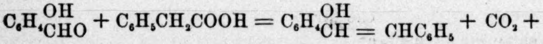
The behavior of a mixture of salicylic aldehyde and phenylacetic acid towards sodium acetate was examined under conditions similar to those employed in the synthesis of stilbene. Equal parts of the aldehyde and acid and about one-third part of anhydrous sodium acetate were well mixed, and the mixture heated in a closed tube for about 12 hours at 200°. Upon opening the tube carbonic acid was evolved, but I found that the reaction in this case was very complicated, it giving rise to a large quantity of resinous matter, from which a crystalline compound could only be obtained with considerable difficulty. Although the proportions of the ingredients of the mixture, as well as the temperature to which they were exposed, were considerably varied, I found that more satisfactory results were not obtained. The contents of the tube, treated as above, were first boiled with water, then with dilute ammonia, and the residue extracted several times with hot alcohol. The infusions were united, and the solution, after standing in an open vessel for some time, deposited a resinous mass. If, on the addition of water to a small quantity of the filtrate from this resinous mass, a crystalline precipitate was obtained, the whole filtrate was treated in a like manner; if, however, the precipitate was of a resinous character, the solution was still allowed to evaporate by exposure to the air, and it deposited a further quantity of the amorphous matter. The addition of water to the alcoholic solution obtained by filtration, was always found to yield a crystalline precipitate, which consisted of small globular masses, and which, for further purification, were dissolved in alcohol, treated repeatedly with animal charcoal, and finally crystallized 4 or 5 times from the same solvent.

An analysis of the substance, dried at 100°, gave: .2182 gr. of substance gave .6849 gr. of CO_2 and .1251 gr. of H_2O.

		Calculated for $C_{14}H_{12}O$.	Found.
C	...	85.72	85.60
H	...	6.12	6.37

The compound crystallizes from alcohol in long, colorless, arborescent needles, which melt at 135–136°, and solidify on cooling. It is insoluble in cold and almost insoluble in warm water. Cold alcohol dissolves it slightly, in warm alcohol it dissolves very readily. The yield of this compound is very small, owing to the large amount of resinous matter formed in the reaction.

Although this compound has not been sufficiently investigated to allow its rational formula to be given with any great degree of certainty, still the analogy which its formation presents to those of the preceding compounds, leads us to consider it as a derivative of stilbene, in which case the formula is expressed rationally by  $C_6H_4\genfrac{}{}{0pt}{}{OH}{CH=CH-C_6H_5}$, and the compound is ortho-oxystilbene, its formation being according to the equation:



$$C_6H_4\genfrac{}{}{0pt}{}{OH}{CHO} + C_6H_5CH_2COOH = C_6H_4\genfrac{}{}{0pt}{}{OH}{CH=CHC_6H_5} + CO_2 + H_2O.$$

I have, furthermore, made numerous experiments on the action of sodium acetate on a mixture of benzoic aldehyde and succinic acid, but without satisfactory results. The product formed was a greenish-yellow resin, from which a crystalline compound was only once obtained, which I will not describe, since all further experiments to ascertain the precise conditions under which it was formed were without result.

BUFFALO, N. Y., *Oct.* 11, 1879.

ON A NEW METHOD FOR THE SEPARATION AND SUBSEQUENT TREATMENT OF PRECIPITATES IN CHEMICAL ANALYSIS.[*]

By F. A. Gooch.

The introduction of Bunsen's method of filtration and immediate ignition of precipitates in the moist condition has left little to be desired as regards accuracy of result and rapidity of execution, in the treatment of precipitates which may be submitted to high temperatures in contact with carbonaceous matter. In analytical methods which require that filter-paper and precipitate shall be ignited apart, or dried together at a temperature below the point at which paper begins to char, the same degree of exactness has not, in general, been hitherto attained.

To obviate the difficulty of bringing a paper-filter of ordinary dimensions, particularly when covered with a voluminous precipitate, to a definite condition of desiccation, the sand-filters of Dr. Gibbs and Taylor,[†] the porous cones of Munroe,[‡] and finally the process of reverse filtering, first applied to quantitative work by Carmichael,[§] improved by Casamajor,[||] and thoroughly elaborated by Professor Cooke,[¶] have been successively brought forward.

The latter process gives most excellent results in the separation of precipitates which settle quickly and completely; and, inasmuch as many precipitates which of themselves are not inclined to fall rapidly may be made to do so by proper treatment (by boiling, for example, the addition of ammonium salts, Chatard's[**] method of granulating gelatinous precipitates, or other similar device), the field of usefulness of this process is wide.

The sand-filters in skilful hands, and the porous cones with no more than ordinary care, give accurate results, and possess moreover the advantage of being applicable to the filtration of liquids which quickly destroy woody fibre. The length of time required to dry them thoroughly, and their sensitiveness to atmospheric conditions, are their great drawbacks.

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[*] Presented to the American Academy of Arts and Sciences. Communicated by the Author.

[†] Am. Jour. [2], vol. xliv. p. 215.

[‡] Am. Jour. [3], vol. i. p. 1.

[§] Zeitschr. f. Chem. [N. F.], Bd. 6, p. 481.

[||] Am. Chem. vol. v. p. 441.

[¶] Proc. Am. Acad. Arts & Sci. vol. xii. p. 124.

[**] Am. Jour. [2], vol. 1, p. 247.

For the simple filtration of corrosive liquids without reference to a subsequent estimation of the precipitate, filters of sand, broken glass, garnets, and fibrous asbestus have for a time been used. More recently, asbestus has been moulded into the shape of an ordinary filter: in the dry state by Lœwe,* by rubbing between hollow and a solid wooden cones; in the wet state by Gruner,† by grinding asbestus, mixed in a mortar with water, to a pulp, transferring the mixture to a funnel choked with asbestus, inserting an accurately fitting cone of brass gauze, which presses the asbestus against the walls of the funnel, pouring off the water, carefully removing the cone and drying the layer of asbestus which adheres to the glass. Bœttger ‡ has used filters of gun-cotton; and Bunsen § has devised a filtering apparatus for corrosive liquids to be attached to his pump, which consists of a disc of artificial pumice fitted to a conical tube and packed round its edge with fibrous asbestus.

None of these later-mentioned methods, however, are well adapted to the quantitative estimation of precipitates.

Impressed with the desirability of further improvement in those processes of quantitative analysis which involve the use of dried filters, or the separation of filter and precipitate before ignition, I have had the good fortune, in taking the matter up in turn, to succeed in devising and preparing a felt of anhydrous asbestus, which is capable of filtering liquids with a rapidity and efficiency at least as great as may be obtained by the use of good filter paper; is light, compact, incombustible at the highest temperatures used in analytical processes; is not acted upon by acids (excepting hydrofluoric acid) or alkalies; is sufficiently coherent to resist entirely the disintegrating action of a liquid forced through it under the pressure of the Bunsen pump, and which may moreover be prepared by a very simple process; in short, a filtering material which, in my belief, makes it possible to reach a high degree of accuracy in many analytical processes which hitherto have been none of the best, and to add to those already known new methods which previously have been impracticable.

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* Dingl. pol. Jour. cxlviii. 444.

† Jahresb. Chem. 1869, p. 990.

‡ Dingl. pol. Jour. clv. p. 463.

§ Ann. Ch. Pharm. cxlviii. p. 290.

My mode of preparing and using the asbestus felt is as follows:—

First, white, silky, anhydrous asbestus,* is scraped to a fine short down with an ordinary knife-blade, boiled with hydrochloric acid to remove traces of iron or other soluble matter, washed by decantation and set aside for use.

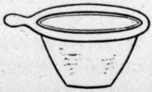

Fig. 1.

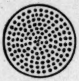

Fig. 2.

Secondly, a platinum crucible of ordinary size, preferably of the broad low pattern (Fig. 1), is chosen, and the bottom (Fig. 2) perforated with fine holes (the more numerous and the finer the better) by means of a steel point; or, better still, the bottom may be made of fine platinum gauze. Next, a Bunsen funnel of the proper size is selected, and—following Munroe's plan for holding his porous cones—over the top a short piece of rubber tubing is stretched and drawn down until the portion above the funnel† arranges itself at right angles to the direction of the stem. Within the opening in the rubber, the perforated crucible is fitted as shown in figure 3, and the funnel is connected with the receiver of a Bunsen pump or other exhausting apparatus in the ordinary manner.

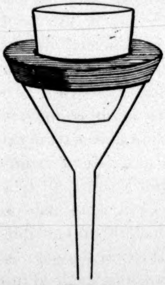

Fig. 3.

To make the asbestus felt, the pressure of the pump is applied, and a little of the asbestus prepared as described, and suspended in water, is poured into the crucible. The rubber and the crucible are held together by the pressure of the vacuum-pump with sufficient force to make an air-tight joint; the water is drawn through, and the asbestus is deposited almost instantly in a close compact layer upon the perforated bottom; more asbestus (if necessary) in suspension as before being poured upon the first, until the layer becomes sufficiently thick for the purpose for which it is intended. Finally, a little distilled water is drawn through the apparatus to wash away any filaments that might cling to the under side, and the filter is ready for use: the whole process occupying less time than is necessary to fold and fit an ordinary paper-filter to a funnel.

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* Note, November 1879. I have found it very hard to procure asbestus of the proper quality from dealers in this country; but it would appear from the fact that several lots imported from Germany at different times have proved to be serviceable, and some of them excellent, that the difficulty is not due to a scantiness in the natural supply.

† Note, November 1879. It is better, as Professor H. B. Hill suggests, to leave a margin of the inner edge projecting upward.

To prepare the filter for the estimation of a precipitate, the crucible with the felt undisturbed is removed from the funnel and ignited. In case the precipitate, to be subsequently collected, must be heated to a very high temperature for a long time, it is better to enclose the perforated crucible with its felt within another crucible; because, in such cases, asbestus felt is apt to curl at the edges, and without such precaution some of the precipitate might drop through the perforations and be lost. For drying at low temperatures, however, and even for ordinary ignitions, a second crucible is unnecessary; but, during the ignition of an easily reducible substance, care must be taken to prevent the contact of unburnt gas with the perforated bottom.

To perform the filtration, the crucible is replaced in the funnel, the pressure applied, and the process conducted precisely as in an ordinary filtration by the Bunsen pump. It is necessary to observe that the vacuum-pump is to be started before pouring the liquid upon the filter. The final drying or ignition, as the case may be, of precipitate and filter is made without difficulty, or need of extra precaution.

When turbid liquids are to be filtered, or gelatinous precipitates to be separated, instead of the perforated crucible, I prefer to use a platinum cone (Figs. 4 and 5), the upper part of foil (to make a tight joint with the rubber fitting of the funnel), the lower of gauze. The method of covering the gauze with felt is identical with that described above. By reason of the larger filtering surface of this apparatus, the tendency to become

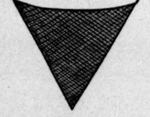
Fig. 4.

clogged is, of course, very much diminished. When subjected to prolonged ignition, the gauze cone is encircled within a crucible or a cone of platinum foil.

In operations in which platinum is liable to receive injury, a porcelain crucible, with a perforated bottom, may be used; but recourse to this is rarely necessary, particularly when one may use the gauze cone protected, as it is, by asbestus felt; moreover the perforation of porcelain with numerous fine holes is a matter of considerable difficulty and expense.

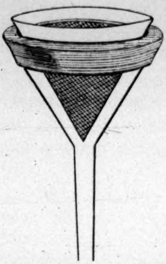

Fig. 5.

Asbestus felt may be also used in the process of reverse filtering, it being merely necessary to dip the platinum rose into the asbestus mixture, after starting the vacuum-pump, in order to make the felt. The rose, with the felt attached, and the vessel in which the precipitate is collected, are to be weighed together, both before and after filtration.

Nothing can be simpler than the whole method of preparation and use of the apparatus which I have described, and its efficiency is extremely great. Clean water may, under the pressure of a Bunsen pump, be passed through a gauze cone coated with asbestus felt, which exposes a filtering surface of twenty-four square centimetres (nearly the same as that of a paper filter eight centimetres in diameter, when folded in the ordinary manner), with ease at the rate of a litre per minute. When the filtering surface is less, the rapidity of filtration is, of course, somewhat diminished, but, supposing the asbestus used to be of the best quality, always exceeds that of paper of the same dimensions. When the felt is deposited upon gauze, the layer may be surprisingly thin and yet be efficient enough for all ordinary purposes. If the layer of felt be quite thick, the filtrate from baric sulphate freshly precipitated in the cold, may be made to pass through clear. But the great superiority of asbestus felt lies in its constancy of weight, whether dried at high or low temperatures, the rapidity with which it may be safely and completely dried, and its refractoriness as regards acids (excepting hydrofluoric acid) and alkalies. These advantages appear most prominently in processes which involve the separation and desiccation:—

First, of precipitates which (like K_2PtCl_6, $[Hg_2]Cl_2$) must be dried at low temperatures, on account of a tendency to decompose spontaneously at high temperatures;

Secondly, of precipitates which (like Sb_2S_3, $PbSO_4$, $ZnCO_3$) have usually been dried slowly and tediously at low temperatures, or have been separated from the filter before ignition, to avoid the danger of reduction by heating in contact with carbon;

Thirdly, of precipitates which (like $(NH_4)_2Mg_2P_2O_8$, $(NH_4)_2Mn_2P_2O_8$) may be ignited in contact with carbon, but which make its complete combustion difficult.

In all cases, the time required to dry or ignite precipitate and filter is a minimum, inasmuch as heat may be applied as soon and to as high a degree as the precipitate itself will permit. Even in processes in which paper filters find their most convenient application, paper has generally no superiority over asbestus felt.

To illustrate the cohesiveness and refractory nature of the felt, I append the account of a single experiment. All of the liquids used had been previously filtered, excepting the distilled water with which the filter was washed, after the passage of each liquid. This precaution was considered unnecessary in the case of the water; but, if it had been taken, the slight *increase* of weight which was observed during the experiment would probably have been prevented.

Weight, in grammes, of crucible and felt, after ignition	20.2020
after second ignition	20.2020
after passing 100 cm^3 of strong HCl through the filter *ten* times, washing and igniting	20.2020
after passing 100 cm^3 of strong HNO_3 through the filter *ten* times, washing and igniting	20.2021
after passing 100 cm^3 of strong H_2SO_4 through the filter *five* times, washing and igniting	20.2022
after passing 100 cm^3 of a mixture of strong H_2SO_4 and water in equal parts, *ten* times through the filter, washing and igniting	20.2024
after passing 100 cm^3 of water, containing in solution 50 grammes of NaOH *ten* times through the filter, washing and igniting	20.2028
Weight of crucible	20.1932
" " felt	.0088

The whole process, involving, in all, the filtration of five litres of liquid (of which one litre was viscous), more than forty changes of the receiver, together with the ignition, cooling, and weighing of the crucible and felt seven times, was completed in two hours and ten minutes. The disc of felt was eleven millimetres in diameter.

ON SEVERAL SPANISH MINERALS.

By F. A. Genth, Jr.

During spring of last year I had occasion to examine some minerals which had been presented to the University of Pennsylvania by the Spanish Government, at the close of the late Centennial Exhibition.

Among these were two of more than ordinary interest.

The first, which formed the principal portion of an ore, and was indicated in the Spanish catalogue as "Sulfo-arseniuro de nikel," from Benahanis, Province of Malaga, proved to be a cobaltiferous gersdorffite; the other, labelled "Sulfuro de antimonio argentifero," from the Province of Huelva, was found to be a massive variety of jamesonite.

Cobaltiferous Gersdorffite.

The gangue-rock, in which the gersdorffite occurs, is calcite. This is found in large, white, crystalline, cleavable, masses, oftentimes so intimately mixed with the gersdorffite that they seem to be but one mineral of a light grey color. It then has a conchoidal fracture.

When placed in dilute hydrochloric acid the calcite dissolves, and the gersdorffite remains behind as a very fine crystalline powder, the particles of which are too small and indistinct for one to recognize any definite form. Granular massive. $H = 5$; Sp. gr. $= 5.856$. Lustre metallic, but somewhat tarnished. Streak greyish-black. Color grey.

Before the blowpipe, in the closed tube, it gives a yellowish-brown sublimate of sulphide of arsenic, and sulphur above the same. In the open tube fumes of sulphurous oxide are given off, and a white crystalline sublimate of arsenious oxide is formed on the cold parts of the tube. On charcoal it is reduced to a white, bright, and brittle globule, with the emission of arsenical and sulphurous fumes.

Treated with successive portions of borax, the iron, cobalt, and nickel reactions are produced.

It is not acted upon by hydrochloric acid, but is decomposed by nitric acid, with the separation of sulphur and arsenious oxide. The solution is of a brownish green color.

An analysis of the gersdorffite, in which the cobalt was separated from the nickel by KNO_2, gave the following result:

S	...	22.01
As	...	39.71
Fe	...	1.12
Ni	...	24.83
Co	...	12.54
Cu	...	0.25
		100.46

which corresponds with the formula $R(S, As)_2$ in which the Ni : Co as 2 : 1 and the S : As in the ratio of 14 : 11, which would make it a gersdorffite, very rich in cobalt.

Associated with the gersdorffite and calcite are,

(*a*) Chalcopyrite, mostly massive, often intimately mixed with the gersdorffite; generally tarnished.

(*b*) Erythrite, in beautiful, but very small rose colored crystals and crystalline scales, some showing a monoclinic form. The color is less blue than is generally the case, but a qualitative test gave only cobaltous oxide, arsenic pentoxide, and water.

(*c*) Pharmacolite, in globular botryoidal masses, of a pale reddish white, or flesh-red, color, due to the admixture of some arsenate of cobalt; structure radiating; lustre silky.

(*d*) Lavendulite, a beautiful, pale, ultra-marine-blue mineral, forming a very thin coating. Very rare; only one of the specimens shows a minute portion of lavendulite.

(*e*) Olivenite, (?) in globular aggregations of a deep green color; very probably olivenite, as it gave the reaction for copper.

(*f*) Aragonite, in white elongated needles and spear-shaped crystals, radiating from common centres, but too small and indistinct to determine their form. A qualitative test gave CaO and CO_2.

Jamesonite.

The "Sulfuro de antimonio argentifero," from the Province of Huelva, is a mineral which is indistinctly crystalline, the particles showing lamination. Massive. Fracture uneven. H = 2.5. Sp. gr. = 5.467; soils paper. Lustre metallic. Color dark steel grey. Streak almost black. Opaque.

Before the blowpipe it fuses easily, giving a sublimate of sulphur and antimonious sulphide in the closed tube, and a white sublimate of antimonious oxide, and sulphurous oxide, in the open tube. On charcoal, with soda, it yields a metallic button of lead and antimony, surrounded by a white incrustation which is yellow nearer the assay.

Soluble in hydrochloric acid, with the evolution of hydrogen sulphide, and separation of plumbic chloride; in nitric acid with the separation of antimonious oxide, plumbic sulphate, and sulphur.

The mineral appeared to be homogeneous, with the exception that a considerable quantity of pyrite was disseminated throughout the entire mass, so that it was impossible to obtain material for analysis perfectly free from it.

There was also present a yellowish white soft mineral, with a waxy lustre, which was not further examined.

The analysis gave the following result:

Fe	...	5.95
Ag, Cu	...	0.28
Pb	...	38.29
[*] Sb	...	33.15
S	...	23.60
		101.27

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[*] Sb = 122.

Another Sb determination gave 33.27 per cent.

This would give the formula $(Pb\ Fe)_2\ Sb_2S_5$, together with a small quantity ($\frac{1}{15}$) of pyrite. After deducting the pyrite, the pure mineral has the following composition:

Sb	...	34.03
S	...	22.31
Pb	...	38.49
Fe	...	5.16
		99.99

CHEMICAL LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA,
WEST PHILADELPHIA, *November 14th*, 1879.

A METHOD FOR ESTIMATING BISMUTH VOLUMETRICALLY.

BY M. KUHARA,

Fellow in Chemistry, Johns Hopkins University.

Bismuth may be estimated gravimetrically as $2BiAsO_4.H_2O$ (dried at 100°–120°), by precipitating its nitric acid solution with arsenic acid or sodic arseniate, collecting the precipitate on a weighed filter after washing it by decantation, and weighing the filter and precipitate together.* In carrying out this process of estimation, however, various difficulties are met with.

It occurred to me that by taking advantage of Bœdeker's method for the estimation of arsenic acid† the gravimetric method above referred to might be converted into a volumetric. My hopes were completely realized, as the new method gives very accurate results.

The method was based upon the precipitation of bismuth, as $BiAsO_4$, from its nitric acid solution, by adding a measured quantity of standard solution of disodic arseniate in slight excess, and upon the determination of the amount of residual arseniate by means of standard uranic nitrate. In carrying out the estimation, the nitric acid solution of bismuth under examination must be free from hydrochloric acid, as well as substances precipitable by arseniate. Before entering upon the process of actual analysis, the amount of bismuth in a solution to be examined was approximately ascertained by the same method as that employed in the actual analysis.

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* H. Salkowski, Jour. pr. Ch. 104, 170. Zeit. f. anal. Ch. 8, 205.

† Fresenius Quant. Analysis, p. 256.

Now a convenient quantity of the solution under examination was taken, a slight excess of disodic arseniate solution whose exact strength had been previously ascertained by a known weight of bismuth, was added to the solution, which was then agitated well without heating, and the mixture was set aside for a time to complete the reaction. The mixture containing the precipitate was rendered slightly alkaline with ammonia and then slightly acid with acetic acid. Now uranium solution, the relative strength of which as compared with that of arseniate had been previously ascertained, was allowed to run in from a burette very slowly, the mixture having been constantly well agitated to complete the reaction. The end of the reaction was recognized in the ordinary manner by means of ferrocyanide of potassium. From the amount of uranium solution used the excess of arseniate can be calculated; and from the actual amount of arseniate found by subtracting the excess from the whole amount taken, the quantity of bismuth can be easily calculated.

The following results were obtained:

For the standard solution of arseniate about 20.87 gr. of disodic arseniate were dissolved in 1 litre of water, and for the uranium solution about 35.6 gr. of uranic nitrate.

Relative strengths of arseniate and uranium solutions:—

		C. c. of arseniate taken.	C. c. of uranium solution used.
(1)	...	10	10.0
(2)	...	10	9.9
(3)	...	10	10.1
(4)	...	10	10.2
		—	——
		Mean =	10.06

1 c. c. of arseniate = 1.005 c. c. of uranium solution.

Standardization of arseniate in terms of bismuth :—

	Grams of bismuth taken.	C. c. of arseniate taken.	C. c. of uranium solution used.
(1)	.10	13	6.0
(2)	.10	13	5.9
(3)	.10	13	5.7
(4)	.10	13	5.7
(5)	.10	13	5.7

Mean = 5.8

1 c. c. of arseniate = 0.01369 gr. of bismuth.

The following results were obtained by using a known weight of bismuth :—

	C.c. of Bi. taken.	C. c. of arseniate taken.	C. c. of uran. solution used.	C. c. of arseniate used.	Bismuth found.
(1)	.125	12	3.3	8.7	.119103
(2)	.125	12	3.2	8.8	.120472
(3)	.125	12	3.3	8.7	.119103
(4)	.125	12	3.3	8.7	.119103
(5)	.125	12	3.1	8.9	.121841
(6)	.125	12	3.0	9.0	.123210
(7)	.125	12	2.9	9.1	.124579
(8)	.125	12	2.9	9.1	.124579
(9)	.125	12	2.9	9.1	.124579
(10)	.125	12	3.0	8.7	.119130

These results were not quite satisfactory, so other experiments were made.

Uranic nitrate solutions of different strengths were prepared, and that containing 43.2 gr. of crystallized uranic nitrate in one litre of water was found to give the best results. The strength of the arseniate solution remained the same.

Relative strength of sodic arseniate and uranic nitrate :—

	C. c of arseniate taken.	C. c. of uran. solution used.
(1)	10	8.95
(2)	10	8.90
(3)	10	8.80

Mean = 8.88

1 c. c. of uranic solution = 1.126 c. c. of arseniate.

Standardization of arseniate in terms of bismuth by using uranic nitrate solutions of different strengths:—

		Grams bismuth taken.	C. c. of arsen. taken.	C. c. of uran. used.	C. c. of arsen. used.
(1)	...	.1	13	4.95	7.427
(2)	...	.1	13	5.10	7.258
(3)	...	.1	13	5.15	7.201

Mean = 7.295

1 c. c. of arseniate = .0137 gr. of bismuth.

The following results were obtained by using known weights of bismuth:—

		Grams bismuth taken.	C. c. of arsen. taken.	C. c. of uran. used.	Excess of arsen. found.	C. c. of arsen. used.	Bismuth found.	Difference. Gain or loss.
(1)	..	.125	12	2.57	2.893	9 107	.124766	+.000240
(2)	..	.125	12	2.60	2.927	9.073	.124300	+ 000700
(3)	..	.125	12	2.60	2.927	9.073	.124300	+.000700
(4)	..	.125	12	2.55	2.871	9 129	.125067	—.000067
(5)	..	.125	12	2.56	2.882	9.118	.124916	+.000084
(6)	..	.125	12	2.60	2.927	9.073	.124300	+.000700

NEW RESULTS IN ELECTROLYSIS.

By Edgar F. Smith.

Succeeding the publication of a short article upon the electrolytic estimation of cadmium,* the idea suggested itself that perhaps the rarer metals would disclose new facts as regarded their behavior toward the electric current. In short, I concluded to experiment upon a series of inorganic salts in this direction, with what result the following lines will show.

Beginning first with uranium, I gradually obtained results which were highly interesting; yielding among others a new method of estimating this element, and at the same time an excellent separation of it from the alkalies, alkaline earths, &c.

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*Am. Jour. Sciences & Arts, Jan. 1879.

A platinum crucible containing about 10 c. c. of water, having in solution .1000 gr. of impure uranic acetate, was connected with the zinc pole of a bichromate battery of two cells, (pint flasks), while to the carbon pole was attached a copper wire carrying a platinum spiral, which was immersed in the cold aqueous solution. Upon allowing the current to act for about one quarter of an hour, a slight iridescent coating was perceptible upon the crucible sides. Thinking that heat might be of avail, I placed the platinum receptacle upon a water bath and heated the contents of the latter to about 60° -70°C. Very soon the crucible sides became covered with a thin pale film, which gradually grew thicker, while the liquid slowly lost its yellow color. Finally, when the solution was colorless, I perceived a change in the yellow deposit; it was gradually assuming a black color. The action of the battery was continued until the entire yellow colored mass had changed to black. The crucible was now disconnected from the battery, the clear liquid decanted through a filter and tested for uranium, but not any detected.

The black deposit was hastily examined, but nothing definite learned in regard to its composition. Not more than one and a half hours were required to precipitate the uranium and convert it into the black colored deposit.

A second portion of uranium acetate was treated as just mentioned, and when I had fully convinced myself that the precipitation of uranium in this form was complete, I took steps to procuring the black deposit in larger quantities in order that I might be able to learn its true composition.

To the solutions with which I experimented I invariably added a little free acetic acid, in order that the yellow hydrated uranic oxide might not separate too rapidly, and thus become mixed with the black, and escape conversion into the latter. To render this certain, I always treated the black deposit with warm dilute acetic acid before allowing it to dry.

The coating upon the crucible appeared black in color, and adhered tenaciously to the sides. In all experiments the platinum vessel in which the deposition occurred was placed on a water bath, and the temperature previously mentioned carefully preserved. From solutions of about .1 gr. substance in 10 c. c. H_2O the precipitation is most rapid.

When a rather large quantity of material had been obtained, it was dried by standing over sulphuric acid several days, and then subjected to analysis.

Analysis of Black Deposit.

1. 1.2061 gr. substance were placed in a carefully weighed platinum boat = 2.3968 gr., and this then introduced into a perfectly dry combustion tube of Bohemian glass, to one end of which was attached a calcium chloride tube weighing 21.2554 gr. After strong ignition in a combustion furnace, with a stream of dry oxygen gas playing over the substance, the calcium chloride tube was detached and reweighed. Its weight now equalled 21.3906 gr., showing an increase of 0.0542 gr. due to water. The platinum boat was carefully removed from the tube and weighed a second time.

3.5470 gr. represented the Ur_3O_4 + boat.
2.3968 " " plat. boat alone.
1.1502 " " Ur_3O_4

The first weight of boat + substance = 3.6029 gr.
and this minus the boat + Ur_3O_4 = 3.5470
.0559 gr.

which represents loss sustained upon ignition. The slight difference between this loss and the actual increase of the calcium chloride tube may be attributed to error in weighing, or perhaps to a slight loss of oxygen suffered by the uranium protosesquioxide.

The 1.1502 gr. Ur_3O_4 contained 0.9765 gr. uranium, corresponding to 80.96 per cent. Ur. The increase in weight of the calcium chloride tube equalled .0542 gr. water, corresponding to 4.63 per cent. H_2O.

Analysis of Black Deposit.

2. The platinum boat + sub. dried over sulphuric acid as before weighed	3.5141 gr.
Platinum boat — sub. = ...	2.3968 gr.
	1.1451 gr.

material for analysis. This, upon ignition in a combustion tube, as described in (1), gave the following result:

Wt. of $CaCl_2$ tube + H_2O 21.3189 gr.
" " " − " 21.2738 gr.
.0451 gr.

represent the H_2O.

The platinum boat carefully removed and reweighed, gave, weight of boat + Ur_3O_4 = 3.4645 gr., and 3.5141 (first weight of boat + sub.) minus 3.4645 = .0496 = weight of H_2O.

The slight difference here again between the amount of water found by actual increase in the weight of the calcium chloride tube and that indicated by the loss in weight of the boat is, unquestionably, to be ascribed to the loss of oxygen on the part of the Ur_3O_4.

Now, .0451 gr. H_2O = 4.05 per cent. H_2O, and 3.4645 gr. (Ur_3O_4 + boat) minus 2.3968 gr. (wt. of boat) = 1.0677 gr. Ur_3O_4 = .9065 gr. uranium, corresponding to 81.13 per cent. Ur.

The result of analysis would then be 81.13 per cent. uranium, 4.05 per cent. water, and 14.82 per cent. oxygen, calculated from the weight of protosesquioxide of uranium obtained.

Upon calculating with a view of arriving at the chemical formula of the oxide from the above analysis we get:

Analysis 1.

$$\left.\begin{array}{llll} 80.96 & \text{per cent.} & \text{Ur} & \div\ 120 = 67 \\ 14.39 & \text{"} & \text{O} & \div\ 16 = 89 \\ 4.63 & \text{"} & H_2O & \div\ 18 = 25 \end{array}\right\} \div\ 11 = \begin{array}{ccc} 6 & & 3 \\ 8 & \text{or} & 4 \\ 2 & & 1 \end{array}$$

Analysis 2.

$$\left.\begin{array}{llll} 81.13 & \text{per cent.} & \text{Ur} & \div\ 120 = 67 \\ 14.82 & \text{"} & \text{O} & \div\ 16 = 90 \\ 4.05 & \text{"} & H_2O & \div\ 18 = 22 \end{array}\right\} \div\ 11 = \begin{array}{ccc} 6 & & 3 \\ 8 & \text{or} & 4 \\ 2 & & 1 \end{array}$$

The numbers 3 : 4 : 1 would therefore represent the ratio in which the several constituents are present, or the black oxide as thrown out by the battery and as proven by analysis may be expressed by the formula $Ur_3O_4H_2O$, which requires the following:

81.44 per cent. uranium
4.07 " water
14.49 " oxygen

The black material never experienced any loss in weight by standing over sulphuric acid.

All the analyses which I have since made point to the above composition as being correct. When the dark deposit is dissolved in sulphuric acid, and potassium permanganate allowed to pass into the solution, a considerable quantity of uranous oxide was shown to be present. A number of qualitative tests confirmed this.

In some instances in the course of my work I noticed that the yellow hydrated sesquioxide remained on the crucible sides, and upon ignition, passed first into the anhydrous Ur_2O_3, then into Ur_3O_4. The occurrence of the sesquioxide will always be observed, unless the electric current is permitted to pass into the solution until the deposition on the crucible walls becomes thoroughly dark in color. Of course this precaution is not necessary when a simple determination of the uranium in solution is solely regarded.

To discover how reliable this method of precipitation would be, various salts were prepared and the uranium determined by this means.

Double Acetate of Uranium and Sodium.

The properties of this compound are sufficiently well known not to require a detailed description here. After obtaining it in the characteristic hemihedral form, (tetrahedrons), the crystals were reduced to a powder, carefully dried and analyzed with the following results:

1. 0.1575 gr. double acetate were dissolved in about 10 c. c. water in a platinum crucible. The latter was placed upon a water bath, the temperature of which was about 70°C, and the connections made with two cells of a potassium bichromate battery. In the course of two to three hours the uranium was completely thrown out of solution as protosesquioxide, forming a black deposit upon the crucible sides. The crucible was now disconnected, the liquid filtered through a small filter, thus catching any loose particles of the oxide. After washing the deposit several times with hot water, the crucible and contents (the small filter having been added) were dried upon a warm plate and then ignited. Upon cooling the weight was taken. Found .0943 gr. Ur_3O_4, which equalled .08006 gr. uranium, corresponding to 50.83 per cent. Ur.

The filtrate and washings were evaporated and tested for uranium, but none was detected.

2. 0.1240 gr. material treated as just described above, gave .0743 gr. Ur_3O_4, corresponding to .0630 gr. uranium = 50.80 per cent. Ur. The time required for complete separation was the same as in (1).

3. 0.1461 gr. substance gave, after three hours' action of battery, .0815 gr. Ur_3O_4, equal to .07429 gr. uranium, corresponding to 50.84 per cent. Ur.

A combustion of the salt was then made to obtain the amount of carbon and hydrogen.

1. .2853 gr. dried double salt gave, upon burning with lead chromate in a stream of oxygen, .1640 gr. CO_2 = 15.66 per cent. carbon and .0580 gr. H_2O = 2.26 per cent. hydrogen.

2. 0.2385 gr. substance treated as in (1) gave .1401 gr. CO_2 = 16.00 per cent. carbon and .0490 gr. H_2O = 2.26 per cent. hydrogen.

These results show that this double salt is apparently a union of one molecule of uranium acetate with a like amount of sodium acetate. An examination of the theoretical and found percentages would indicate this:

$(C_2H_3O_2)U_2O_2$, $C_2H_3O_2Na(Ur = 120)$, requires:

				Found.	
50.84	per cent.	Ur	50.83	50.80	50.84
4.87	"	Na			
15.25	"	C	15.66	16.00	
1.90	"	H	2.24	2.26	
27.11	"	O			

Double Acetate of Uranium and Potassium. Uranium Determination.

1. 0.1090 gr. salt yielded .0610 gr. Ur_3O_4, which correspond to 47.43 per cent. uranium. The same dilution was observed here as in the case of the sodium and uranium acetate. Time, a little over two hours. The filtrate was free from uranium.

2. .2122 gr. double salt gave, after a little more than two hours, .1195 gr. Ur_3O_4, corresponding to 47.7 per cent. Ur.

A combustion of the salt gave the following:

0.8250 gr. salt carefully burned with lead chromate afforded .4192 gr. carbon dioxide, equalling .1143 gr. carbon, corresponding to 13.85 per cent. C; and .14099 gr. H_2O = .0156 gr. hydrogen or 1.87 per cent. H.

$(C_2H_3O_2)_2U_2O_2, C_2H_3O_2K + 2H_2O$ requires:

		Found.
Carbon	14.22 per cent.	13.85 per cent.
Hydrogen	1.77 "	1.87 "
Uranium	47.42 "	47.43 — 47.7

The ratio of the acetates in this salt is also 1 : 1.

Double Acetate of Uranium and Barium.

This salt carefully prepared presents fine, shining, light yellow colored spangles. Only two determinations of the uranium by the battery were made, inasmuch as these were deemed sufficient to show that the method was perfectly applicable in such instances. In the first analysis the salt was not as pure as in (2); and this therefore would account for the low result in that instance.

1. 0.1090 gr. double salt gave .0528 gr. Ur_3O_4, corresponding to 41.11 per cent. uranium. Two hours were necessary for the deposition.

2. 0.1134 gr. salt gave .0556 gr. Ur_3O_4, equalling 41.63 per cent. uranium. About two hours were required for the complete separation of uranium oxide and its conversion into protosesquioxide.

3. *Barium Estimation.* 0.1835 gr. salt gave .0384 gr. $BaSO_4$ = .0225 gr. Ba, corresponding to 12.2 per cent. Ba.

The formula $2(C_2H_3O_2)_2U_2O_2; (C_2H_3O_2)_2Ba + 6H_2O$ requires:

		Found.
Uranium	41.99 per cent.	41.11 and 41.63 per cent.
Barium	11.98 "	12.20.

This method has also been employed in the analysis of certain silicates containing uranium, and afforded excellent results.*

From the preceding analyses it will be seen that the method admits of a good separation of uranium from the alkalies and alkaline earths. The usual methods are more tedious and certainly not more accurate.

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* This Journal, Vol. 1, No. 2, p. 88.

The method was extended to other salts of uranium with a view of ascertaining their behavior towards the electric current, and as they may perhaps be of interest, I append the results.

Uranium Nitrate, containing but five molecules of water, was first examined. 0.1200 gr. material dissolved in water in a small platinum crucible, and in the course of about three hours—the current being energetic—the precipitation was complete, and I obtained .0698 gr. Ur_3O_4, corresponding to .05926 gr. Ur or 49.38 per cent. Ur. The amount required theoretically 49.37 per cent. Ur. Free acid was not found in the solution.

I spent considerable time in endeavoring to throw out the protosesquioxide from a neutral solution of the chloride of uranium. The precipitation was indeed effected, only, however, after a number of hours, which of course rendered this salt useless for practical determinations. A constant liberation of chlorine gas was noticeable.

A neutral solution of the sulphate was experimented upon, but the precipitation proved to be very slow.

The double formate of uranium and sodium was made, and in aqueous solution subjected to the action of the battery. The uranium was thrown out as protosesquioxide as in the double acetates.

A solution of the double tartrate of uranium and sodium was evaporated, and permitted to stand for hours. Crystals were not formed, only a gelatinous mass remained. This salt was redissolved, and to the aqueous solution an excess of alcohol added, which caused the precipitation of the double tartrate as a light yellow-colored flocculent mass. After washing with alcohol the compound was dried and a weighed quantity dissolved in water. The aqueous solution was then brought in contact with the battery, but even at the expiration of two days' action of the electric current there was not any uranium precipitated.

The double citrate of uranium and sodium, prepared as the preceding salt and treated in a similar manner, gave like result. The salt is soluble in warm alcohol.

Molybdenum.

Molybdenum in the form of ammonium molybdate in aqueous solution was placed in a platinum crucible, and the latter connected with a two-celled bichromate battery (see Uranium). The current was allowed to act upon both cold and warm solutions. In a very short time a beautiful iridescence appeared upon the crucible walls, and as the action continued the deposit gradually became thicker and black in color. Just here I might add that if very dilute solutions of ammonium molybdate be treated in this way, an exceedingly thin and durable coating can be deposited upon metallic surfaces. Further investigation may perhaps render this of practical value.

I made several efforts to learn whether molybdenum could or could not be thrown out of solution — neutral or ammoniacal—completely by this method. One experiment in which 0.2000 gr. molybdic acid were dissolved in aqua ammonia, required for complete separation of the black deposit about one hundred hours. The liquid from the deposit, after the addition of nitric acid, was treated with sodium phosphate, but not the slightest trace of ammonio-phospho-molybdate was observed.

Ordinarily the black deposit appeared to form rapidly, but I soon observed that, after the coating had attained a certain thickness, the galvanic action almost ceased. Upon the addition of water to the solution, and thus exposing a fresh surface, the action was revived. This would indicate that the dark deposit was a poor conductor. Even when a large surface was exposed, the deposition, although complete, was so very slow that this method of determination was practically of little value.

The deposit was invariably washed very carefully with water and dried by exposure to the air. In acids it is very slowly soluble. The solution in hydrochloric acid diluted with water, possessed a brownish pink color. Ammonium hydrate precipitated from the same a brown mass. The deposit ignited in a closed crucible was converted into beautiful colorless leaflets of molybdic acid.

I prepared a rather large quantity of the black material and analyzed it, and found it to be the hydrate oxide.

Water Determination.

The air-dried substance was weighed in a platinum boat, and the latter then placed in a carefully dried Bohemian combustion tube, to one end of which a weighed calcium chloride tube was attached. Dry carbon dioxide was conducted through the same, and when the air had been expelled the tube was brought to low redness; the passage of carbon dioxide being continued until the end of the operation.

.1310 gr. air-dried material treated as just described, gave .0250 gr. water, corresponding to 19.08 per cent. H_2O.

The residue in the boat possessed a color very similar to potassium permanganate. It was then treated with strong nitric acid in a beaker, and gradually converted into molybdic acid, ammonium hydrate added, and the solution then brought to boiling. When the excess of ammonia had been expelled, a dilute solution of lead acetate was added in slight excess. The ebullition was continued until the precipitate became granular. This it did in a few moments. It was then allowed to subside, the supernatant liquid filtered, the precipitate slightly washed, dried and weighed.

1. .0903 gr. ignited material treated as just mentioned, gave .2766 gr. lead molybdate, corresponding to .0722 gr. Mo = 79.95 per cent.

2. .1161 gr. ignited substance gave .3643 gr. lead molybdate, equivalent to .0922 gr. molybdenum = 79.60 per cent. Mo.

These results approach very closely those required by molybdenum oxide, and this unquestionably is the composition of the black deposit.

$Mo_2O_3.3H_2O$ requires 18.36 per cent. H_2O, and the analysis above gave 19.00 per cent. The ignited residue gave 79.95 per cent. and 79.60 per cent. molybdenum, and the anhydrous Mo_2O_3 requires 79.96 per cent. Mo.

Tungsten.

Several salts of tungstic acid were prepared and studied. Ammonium tungstate (.1000 gr. to about 30 cc. of water) was placed in a platinum crucible, about which circled the wire from the zinc pole of a two-celled bichromate battery, while into the solution dipped a platinum spiral attached to the copper wire leading from the carbon pole. There was a brisk evolution of gas, which continued for twelve hours, without any visible alteration of the tungstate solution. The same result attended the action upon a sodium tungstate solution. After boiling a portion of powdered sodium tungstate with acetic acid, and allowing the current to pass through the solution, the liquid at once acquired a deep blue color, and gradually a very thin blue deposit formed on the crucible walls. By prolonged action of the current this was in part altered to brown, and on exposure to the air the latter slowly passed back to blue. I never succeeded in getting enough material for analytical purposes, although these were really superfluous, the blue deposit being undoubtedly the W_2O_5 oxide ordinarily found in the reduction of tungsten solutions, while the brown was probably $W(OH)_4$ (?)

Vanadium.

Employing a solution of ammonium vanadate and having the same battery connection as in tungsten, I noticed, after brief action of the current, that the originally colorless liquid became yellow and gradually blue or green-yellow. Not any other change was observed.

With vanadium chloride like results were got. There was always a strong evolution of chlorine.

With the sulphate (excess of acid having been removed) I obtained in time an exceedingly minute, dark brown colored deposit, scattered here and there upon the crucible. This was observed, too, when the sulphate solution was mixed with ammonium sulphate in excess.

Didymium.

Neutral sulphate solution did not give any result whatever. With an acetate solution a deposit was noticed upon the zinc pole. This occurred, too, when a nitrate solution was employed. The slight deposition gave reliable reactions for didymium.

Cerium.

Solutions of the nitrate, sulphate, acetate, and double nitrate of cerium and ammonium were experimented with, but the results were unsatisfactory. With a solution of the chloride I had quite a large deposit upon the zinc pole of the battery, which was light yellow in color. There was always some chlorine liberated. The separated oxide acted as a non-conductor, and the precipitation was at the most exceedingly slow. In presence of didymium some of the latter was always co-precipitated. This method of separating cerium could never be of any practical value.

I hope to continue this work upon the behavior of various inorganic salts towards the electric current, as time may permit. The tendency to this field of investigation has induced me to publish the above at this moment.

LABORATORY OF THE UNIV. OF PENN., *Nov.* 21, 1879.

NITROSULPHOBENZOIC ACIDS AND SOME DERIVATIVES.*

BY EDWARD HART.

Certain distinctive properties have been recognized as belonging to each of the three classes of bi-substituted benzenes known as ortho, meta, and para respectively. Ortho compounds melt and boil at lower temperatures than meta and para. Meta compounds come next in this respect, and para highest. This distinction, though a marked one, is not without numerous exceptions. Besides this difference, we recognize certain others more or less general. As a rule, ortho compounds are easily soluble, meta less so, and para least of all. Further, ortho compounds when treated with a mixture of potassium bichromate and sulphuric acid, are either completely destroyed and converted into compounds belonging to other series, or they suffer no change whatever. This does not apply to oxyacids, however, as Remsen† has shown. Probably exception should also be made of amido compounds, which are easily broken up. This last distinctive property of ortho compounds loses much of its value in view of the fact that other oxidizing agents, as, for example, nitric acid and potassium permanganate, do not act in this way, but oxidize all three classes in nearly the same manner.

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*From the Author's Thesis presented to the Johns Hopkins University for the degree of Ph. D.

†Liebig's Annalen, 178, 295.

The object of this investigation has been to determine as far as possible the influence of the position of the substituting groups upon the physical properties of substituted benzenes.

A very large number of bi-substituted benzenes have been prepared, and some of them carefully studied, but the only generalizations with regard to their physical properties that have yet been made are those mentioned at the beginning of this article. The tri-substituted benzenes offer a better field for such work, since here the possibilities of isomerism increase, and the comparison can be made to cover more ground. None of these have been studied with sufficient care for this purpose, and it seemed best to commence by preparing all possible isomers of such a series, fix the position of the substituting groups in each, and then carefully study and compare the compounds themselves and their like derivatives.

The nitrosulphobenzoic acids were chosen for this purpose, for which they have several advantages. (1) They appear to be very stable compounds, a matter of the greatest importance. (2) All three substituting groups are unlike, and therefore a larger number of isomers are possible (in this case 10, while, with all groups alike but 3, with two alike, 6, are possible). (3) They are bibasic acids, hence a larger number of similar derivatives can probably be prepared. (4) They can probably be easily prepared in large quantity if at all, and from a number of different sources, thus making it easier to fix accurately the position of the substituting groups.

Two nitrosulphobenzoic and three amidosulphobenzoic acids had been made before this investigation was undertaken. In none of these were the relative positions of more than two groups known. They had all been prepared in small quantity and not very carefully studied.

By treating metanitrobenzoic acid with fuming sulphuric acid at a temperature near the boiling point of the latter

Mulder* obtained granular crystals of a new salt, which may have been the barium salt of a nitrosulphobenzoic acid, but which he did not examine further. By treating metasulphobenzoic acid with a mixture of fuming nitric and sulphuric acids, Limpricht and Uslar† obtained a nitrosulphobenzoic acid, and by reduction with ammonium sulphide the corresponding amido acid. Griess‡ treated metamidobenzoic acid with sulphuric acid, and obtained two amidosulphobenzoic acids.

Finally, by heating parasulphaminebenzoic acid with a mixture of nitric and sulphuric acids, Remsen§ obtained another of these nitrosulphobenzoic acids, and prepared and analyzed its barium salt. He further indicated a method by which the constitution of the acids then known might be determined, as follows: "Three isomeric nitrobenzoic acids are known, and their constitution is also understood. If it were now possible to introduce the sulpho group in these, compounds would be obtained of which two would be identical with the known nitrosulphobenzoic acids. The constitution of the latter could then be easily determined."

Metanitroparasulphobenzoic Acid.

This is the acid of Remsen, and was prepared according to his directions, except that I used parasulphobenzoic, and not parasulphaminebenzoic acid. Parasulphobenzoic acid was first prepared nearly according to Remsen's directions, from the mixture of toluene sulphoacids by oxidation with potassium bichromate and sulphuric acid. Afterwards I found it much simpler to use potassium permanganate as the oxidizing agent. The yield is in this case much larger, and the process requires much less time. The method adopted after several trials is as follows: 100 gr. toluene is dissolved in the smallest possible quantity of fuming sulphuric acid. The solution is diluted, neutralized with chalk filtered from the calcium sulphate and evaporated to a small bulk. 350 gr. potassium permanganate is dissolved in warm water and added to the solution of the calcium salts; the volume of liquid is then made up to about 5 litres by adding water, and the solution heated over the lamp or on the steam bath until it becomes colorless. The liquid is then filtered from the oxides of manganese and the filtrate supersaturated with hydrochloric acid; barium chloride is then added, which throws down the parasulphobenzoic acid as the acid barium salt. This is purified by crystallizing once from its solution in boiling water. 100 gr. toluene yield about 200 gr. of the acid barium salt.

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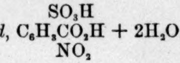
* Liebig's Annalen, 34, 302.

† Liebig's Annalen, 106, 27.

‡ Jour. fuer prak. Chemie, 113, 244.

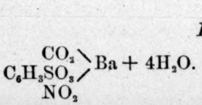
§ Liebig's Annalen, 178, 288.

From the acid barium salt of parasulphobenzoic acid, metanitroparasulphobenzoic acid is prepared by treating it with a mixture of equal parts by weight of fuming nitric and sulphuric acids. 20 gr. acid barium salt require 100 gr. of the mixed acids. The mixture is heated in an evaporating-dish over the lamp until the nitric acid is driven off, diluted, neutralized with barium carbonate, and the barium salt obtained from the filtrate by evaporation. The acid is obtained from the barium salt by exact precipitation of the barium with sulphuric acid.



Metanitroparasulphobenzoic acid, $\mathrm{C_6H_3}\overset{\mathrm{SO_3H}}{\underset{\mathrm{NO_2}}{\mathrm{CO_2H}}} + 2\mathrm{H_2O}$, crystallizes from water, in which it is very soluble, in short, thick prisms. The acid is very slightly soluble in alcohol, and almost completely insoluble in ether, chloroform and carbon bisulphide. The hydrated acid melts at 130°-131°. As the acid blackened and appeared to decompose at a temperature insufficient to drive off all the water, the amount of this was determined by adding a weighed portion to a weighed portion of Iceland spar, and the calcium salt so obtained heated until all water was driven off. In this way .2096 gr. acid + an excess of Iceland spar lost .0715 gr. $H_2O + CO_2$. Theory requires .0725 gr.

Barium Salt.



$\mathrm{C_6H_3}\overset{\mathrm{CO_2}}{\underset{\mathrm{NO_2}}{\mathrm{SO_3}}}\!\!>\!\mathrm{Ba} + 4\mathrm{H_2O}$. This is the salt described by Remsen, the method of preparing which has already been described. The yield from 20 gr. acid barium salt of parasulphobenzoic acid was in one case 15 gr. I am satisfied, however, that it often largely exceeds this. Remsen gives the salt 1½ molecules H_2O. The difference is probably due to the fact that the salt analyzed by Remsen was dried over sulphuric acid, while the figures here given are for the air-dried salt. Experiment shows that the salt loses water very slowly over sulphuric acid, and it seems probable that Remsen's salt was not perfectly dried before analysis. The salt loses a little less than 3 molecules of water over sulphuric acid at the ordinary temperature. It crystallizes in yellow needles which unite at the ends, forming concentric groups. They are moderately soluble in cold and easily in hot water.

I. .2915 gr. salt lost .0435 gr. at 200°, and gave .1497 gr. $BaSO_4$.

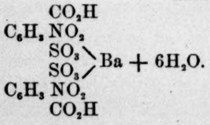
II. .2817 gr. salt lost. 0318 gr. over sulphuric acid, and gave .1451 gr. $BaSO_4$.

III. .3298 gr. salt lost .0382 gr. over sulphuric acid, and .0516 gr. at 235°.

Calculated.			Found.		
			I.	II.	III.
$C_6H_3\left.\begin{matrix}CO_2\\SO_3\\NO_2\end{matrix}\right\}$	245	53.96	...	...	...
Ba	137	30.18	30.00	30.28	...
$4H_2O$	72	15.86	15.68	...	15.65
	454	100.00			
$3H_2O$		12.39	...	11.28	11.59

In the mother liquor from this salt a very soluble yellow salt is contained. The manganese salt of this acid, as well as the zinc salt, appears to crystallize tolerably well, though they are both quite soluble. The entire amount on hand was lost, however, by a mishap before a pure salt had been obtained from it. From an analysis of the impure manganese salt, the acid appears to be dinitrosulphobenzoic, though this is as yet by no means certain.

Acid Barium Salt.



$$\begin{matrix}C_6H_3\begin{matrix}CO_2H\\NO_2\\SO_3\end{matrix}\\C_6H_3\begin{matrix}SO_3\\NO_2\\CO_2H\end{matrix}\end{matrix}\!\!\!\left.\begin{matrix}\\\end{matrix}\right>Ba + 6H_2O.$$

This salt may be obtained either by treating a solution of the neutral salt with hydrochloric acid, evaporating to crystallization, and recrystallizing the product, or by dividing a solution of the neutral salt in two equal portions; exactly precipitating the barium in one portion by sulphuric acid, and adding the other to it. It crystallizes in long prismatic needles, which attain great length under favorable circumstances. The crystals are nearly white. They are easily soluble in water—more soluble than the neutral salt. Solutions of the salt show a very marked tendency to creep up the sides of containing vessels. The salt loses three molecules of water over sulphuric acid.

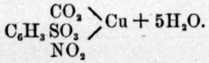
I. .2104 gr. salt lost .0152 gr. over sulphuric acid, .0297 gr. at 180°, and gave .0669 gr. $BaSO_4$.

II. .3758 gr. salt lost .0554 gr. at 210°, and gave .1209 gr. $BaSO_4$.

III. .2481 gr. salt lost .0190 gr. over sulphuric acid, and .0357 gr. at 210°, and gave .0465 gr. $BaSO_4$.

Calculated.			Found.		
			I.	II.	III.
$\left\{C_6H_3\begin{matrix}CO_2H\\NO_2\\SO_3\end{matrix}\right\}_2$	492	66.76	...	...	...
Ba	137	18.59	18.68	18.91	18.72
$6H_2O$	108	14.65	14.12	14.72	14.39
	737	100.00			
$3H_2O$		7.31	7.22	...	7,65

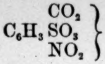
Copper Salt.



$C_6H_3\begin{matrix}CO_2\\SO_3\\NO_2\end{matrix}\!>Cu + 5H_2O$. This salt forms small, hard, bluish-green crystals. It was obtained by evaporating a solution of the salt over sulphuric acid. The salt is difficult to obtain in the pure state, as the solutions deposit a greenish-white substance when evaporated, which appears to be a basic salt. The salt loses two molecules of water over sulphuric acid, and the remainder at a higher temperature.

I. .1945 gr. salt lost .0208 gr. over sulphuric acid.

II. .1285 gr. salt lost .0269 gr. at 250° and gave .0205 gr. Cu.

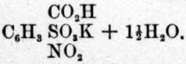
Calculated.			Found.	
			I.	II.
 $C_6H_3\begin{matrix}CO_2\\SO_3\\NO_2\end{matrix}\Big\}$	245	61.50	...	...
Cu	63.4	15.91		15.95
$5H_2O$	90.	22.59	...	20.93
	398.4	100.00		
$2H_2O$		10.45	10.69	...

The result for $5H_2O$ agrees very poorly with the calculated percentage. Inasmuch as the solution was allowed to evaporate over sulphuric acid, and the amount of salt obtained was small, it may have lost a portion of its water. No. I, which represented much the purer portion of the salt obtained, was unfortunately lost before the analysis was completed. The study of the salt was laid by to make room for more important work, and will be again taken up hereafter.

Potassium Salt.

This salt forms small, hard prisms, very soluble in water. No analysis has yet been made.

Acid Potassium Salt.

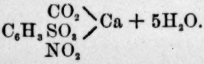

$C_6H_3\begin{matrix}CO_2H\\SO_3K\\NO_2\end{matrix} + 1\frac{1}{2}H_2O$. The salt was obtained by treating a concentrated solution of the neutral salt with hydrochloric acid and recrystallizing the product. It crystallizes in long silky needles, which are moderately soluble in water. On being exposed to the air on filter paper, these crystals break up into granular pieces before they are completely dry. The salt may also be obtained in six-sided plates by allowing a saturated solution to evaporate slowly. The analyses given below were made of the air-dried needles.

I. .2196 gr. salt lost .0191 gr. at 190°, and gave .0611 gr. K_2SO_4.

II. .1826 gr. salt lost .0163 gr., and gave .0503 gr. K_2SO_4.

	Calculated.		Found. I.	Found. II.
$C_6H_3\left\{\begin{matrix}CO_2H\\SO_3\\NO_2\end{matrix}\right\}$	246	78.82	...	...
K	39.1	12.53	12.49	12.37
$1\frac{1}{2}H_2O$	27.0	8.65	8.70	8.92
	312.1	100.00		

Calcium Salt.


$C_6H_3\begin{matrix}CO_2\\SO_3\\NO_2\end{matrix}\!\!>Ca + 5H_2O$. The salt forms large prismatic crystals of a slightly yellowish color, which are tolerably soluble in water. The crystals rapidly effloresce and fall to powder when exposed to the air.

I. .2362 gr. crystallized salt dried rapidly between filtering paper and weighed, lost .0336 gr. over sulphuric acid, and .0207 gr. additional at 250° and gave .0863 gr. $CaSO_4$.

II. .1998 gr. dried over sulphuric acid lost .0234 gr. at 290° and gave .0846 gr. $CaSO_4$.

	Calculated.		Found. I.	Found. II.
$C_6H_3\left\{\begin{matrix}CO_2\\SO_3\\NO_2\end{matrix}\right\}$	245	65.33	...	...
Ca	40	10.67	10.74	...
$5H_2O$	90	24.00	22.99	...
	375	100.00		
$\left\{\begin{matrix}2H_2O\\Ca\end{matrix}\right.$		11.21 12.46	10.21 12.52	11.71 12.45

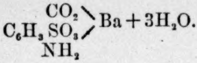
Silver Salt.

No analysis of this salt has yet been made. It is easily soluble in water and crystallizes in large prisms of a yellowish color.

Metamidoparasulphobenzoic Acid.

This is obtained by treating the potassium or ammonium salt of the preceding acid with ammonium sulphide in excess, and evaporating the solution on the water bath until the fumes given off no longer blacken lead paper; upon filtering off the sulphur which has separated, and adding hydrochloric acid, the acid mixed with sulphur is precipitated. It may be purified by converting it into the barium salt, filtering through animal charcoal to remove coloring matter, and reprecipitating with hydrochloric acid. The acid forms a white powder, which, when precipitated from a hot, not too concentrated solution, takes the form of warty masses with a slight tendency to crystallize. It is difficultly soluble even in boiling water, almost entirely insoluble in alcohol, ether and carbon bisulphide. When heated on platinum foil it blackens without previously melting, and gives off fumes with the odor of sulphur dioxide. The watery solution of the acid shows no fluorescence.

Barium Salt.



$C_6H_3\left.\begin{matrix}CO_2\\SO_3\\NH_2\end{matrix}\right> Ba + 3H_2O$. Obtained by treating the acid with water and barium carbonate. It crystallizes in well formed, sharply pointed crystals, which have a very beautiful lustre. A solution of the salt slowly decomposes when evaporated, or even if allowed to stand for a long time, becoming dirty brown or yellow. If such a solution be allowed to crystallize, the crystals are almost black. By filtering through a long tube containing animal charcoal, the coloring matter of such solutions may be removed, and the solutions then show a marked blue fluorescence. This fluorescence is less marked than in the case of another acid and its barium salt, to be presently described.

I. .1712 gr. salt lost .0232 gr. and gave .0953 gr. $BaSO_4$.

II. .2200 gr. salt lost .0296 gr. and gave .1252 gr. $BaSO_4$.

	Calculated.		Found,	
			I.	II.
$\left.\begin{matrix}CO_2\\C_6H_3SO_3\\NH_3\end{matrix}\right\}$	215	52.96	...	...
Ba	137	33.74	32.73	33.46
$3H_2O$	54	13.30	13.55	13.45
	406	100.00		

No. I. was made with a specimen of the salt which had considerable color and which was prepared before the proper method for purification was discovered. No. II. was made with white and quite pure salt.

This acid seems to be identical with one of those made by Griess. I have made the acid of Griess according to his method, and have no doubt that the two are identical, though no analyses have yet been made to test the matter thoroughly. These two methods of preparation—on the one hand from parasulphobenzoic acid, and on the other hand from metamidobenzoic acid—are sufficient proof that the name metamidoparasulphobenzoic acid correctly indicates its constitution. This proof is supported by another, to be considered hereafter.

Paranitroorthosulphobenzoic Acid.

In a preliminary notice* it was stated that by treating paranitrotoluene with sulphuric acid and neutralizing with chalk, two calcium salts had been obtained, one containing **4**, the second 6 molecules of water of crystallization, and which were believed to be the salts of two isomeric acids. A more careful study has, however, led to the conclusion that the first assumption was a mistaken one, and that the two salts differ only in the amounts of water of crystallization which they contain. When treated with phosphorous pentachloride and afterwards with ammonia, they are converted into amides of similar appearance, and melting at precisely the same temperature, 189°. Further, they both yield upon oxidation the same acid—paranitroorthosulphobenzoic. In this connection it may be noticed that Schwanert† has obtained a calcium salt of this acid containing but one molecule of water of crystallization. The proof for the constitution of the above toluenenitrosulphonic acid was given by Ascher.‡ He converted the nitro into an amido acid, replaced the NH_2 group by H by means of Griess's reaction, and by fusing the resulting toluenesulphonic acid with potassium hydroxide obtained salicylic acid, thus showing that the sulpho group occupies the ortho position.

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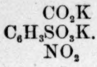
* Ber. der deut. chem. Gesell. X. 1046.

† Liebig's Annalen, 186, 850.

‡ Liebig's Annalen, 161, 1, and Ber. der deut. chem. Gesell. IV. 649.

The potassium salt of the new acid was obtained from the above tolueneparanitroorthosulphonic acid by the oxidation of the calcium salt with potassium permanganate. Paranitrotoluene was dissolved in fuming sulphuric acid. The solution was gently heated and allowed to stand in a warm place, until on diluting with water a clear solution was obtained. The mixture was then diluted, neutralized with chalk, filtered from the calcium sulphate and excess of chalk, evaporated to a small bulk, and to the solution heated upon a water-bath potassium permanganate was added in small quantities at a time, until the solution was not decolorized after 4 or 5 hours' heating. The excess of permanganate was then destroyed by a little alcohol, and the filtrate from the oxides of manganese evaporated until the neutral potassium salt of the new acid crystallized out.

Neutral Potassium Salt.


$C_6H_3\begin{matrix}CO_2K\\SO_3K.\\NO_2\end{matrix}$

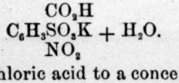
Obtained as above described. The salt is anhydrous and crystallizes in groups of short, thick, opaque prisms, which mostly have a faint yellow color. They are tolerably soluble in cold and more easily in boiling water. The appearance of the crystals is very characteristic.

I. .2698 gr. salt gave .1444 gr $K_2SO_4 = 24.02$ per cent. K.

II. .2733 gr. salt gave .1461 gr. $K_2SO_4 = 24.00$ per cent. K. Theory requires 24.19 per cent. K.

A determination of the sulphur by the method of Fahlberg and Iles, which Dr. Fahlberg kindly made, gave: .31225 gr. salt gave .2125 gr. $BaSO_4 = 9.35$ per cent. S. Theory requires 9.46 per cent. S.

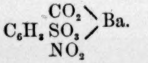
Acid Potassium Salt.


$C_6H_3\begin{matrix}CO_2H\\SO_3K\\NO_2\end{matrix} + H_2O.$

The salt was prepared by adding hydrochloric acid to a concentrated cold solution of the neutral salt. It crystallizes in long, fine white needles, which are only moderately soluble in cold water. By slow evaporation of a saturated solution it may be obtained in thick, short, transparent prisms. The needles were analyzed with the following result: .2339 gr. salt lost nothing over sulphuric acid; .0146 gr. at 150°, and gave .0662 gr. K_2SO_4.

	Calculated.		Found.
$\left.\begin{matrix}CO_2H\\C_6H_3SO_3\\NO_2\end{matrix}\right\}$	246	81.16	...
K	39.1	12.90	12.71
H_2O	18	5.94	6.24
	303.1	100.00	

Barium Salt.



$C_6H_3\begin{matrix}\left.\begin{matrix}CO_2\\SO_3\end{matrix}\right\rangle Ba\\NO_2\end{matrix}$

Very insoluble, small, compact crystals obtained by adding barium chloride to a hot, not too concentrated, solution of the potassium salt. If a saturated solution of the salt be evaporated over the free flame, it separates in very delicate mica-like plates with a beautiful pearly lustre. These plates when air-dried contain about 4 per cent. of water, which they lose in part at low temperatures. All the water, however, is not driven off until a temperature of over 200° is reached. The compact salt also contains water, but in smaller amount (about 3 per cent.) It seems probable therefore that the salt is anhydrous, but very hygroscopic.

I. .1539 gr. salt dried at 220° gave .0941 gr. $BaSO_4 =$ 35.95 per cent. Ba.

II. .1259 gr. salt dried at 250° gave .0775 gr. $BaSO_4 =$ 36.19 per cent Ba.

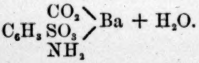
III. .2726 gr. salt dried at 250° gave .1653 gr. $BaSO_4 =$ 35.66 per cent. Ba. Theory requires 35.85 per cent. Ba.

The copper and calcium salts of paranitroorthosulphobenzoic acid have been prepared, but as yet only in small quantities, and no analyses have been made. The copper salt is very soluble and crystallizes in fine blue needles. The calcium salt is also easily soluble and crystallizes in prisms.

Paramidoorthosulphobenzoic Acid.

Made by treating the potassium salt of the above acid with ammonium sulphide, evaporating to dryness on the water bath, and adding hydrochloric acid to the filtered solution. The acid forms long, delicate needles, which are very slightly soluble in cold, more easily in boiling water; almost entirely insoluble in alcohol and ether. Solutions of the acid when evaporated do not become colored. If the solution be made neutral or alkaline, however, decomposition commences if the solution is kept hot, and soon becomes of a dirty brown or black color.

Barium Salt.



$C_6H_3\begin{array}{l}CO_2\diagdown\\SO_3\diagup\\NH_2\end{array}\!Ba + H_2O$. Obtained by adding barium chloride to a solution of the ammonium salt. Very fine needles, which unite to form groups. When a solution of the salt is rapidly evaporated, it separates in mica-like plates with a pearly lustre. The salt is difficultly soluble in water.

I. .1919 gr. salt lost .0100 gr. and gave .1201 gr. $BaSO_4 =$ 5.21 per cent. H_2O and 36.80 per cent. Ba.

II. .1742 gr. salt dried at 220° gave .1156 $BaSO_4 = 39.02$ per cent. Ba. Theory requires, for the hydrated salt, 4.87 per cent. H_2O and 37.03 per cent. Ba; for the dried salt, 38.92 per cent. Ba.

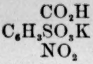
Orthonitroparasulphobenzoic Acid.

This acid was made by treating orthonitrotoluene with fuming sulphuric acid, neutralizing with chalk, evaporating the filtrate to a small bulk, and oxidizing the product by addition of potassium permanganate in small quantities at a time. The solution is filtered from oxides of manganese, neutralized with hydrochloric acid, and evaporated to a small bulk. Hydrochloric acid is then added in excess, which precipitates the acid potassium salt, which is easily purified by recrystallization.

Potassium Salt

Is very soluble in water, by which it is readily distinguished from the corresponding salt of paranitroorthosulphobenzoic acid. No analysis was made.

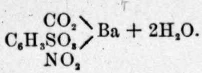
Acid Potassium Salt.



$$\mathrm{C_6H_3}\begin{array}{l}\mathrm{CO_2H}\\ \mathrm{SO_3K}\\ \mathrm{NO_2}\end{array}$$

Anhydrous prismatic plates, which are tolerably soluble in hot, less in cold water. .1980 gr. salt gave .0599 gr. K_2SO_4 = 13.58 per cent. K. Theory requires 13.71 per cent. K.

Barium Salt.



$$\mathrm{C_6H_3}\begin{array}{l}\mathrm{CO_2}\diagdown\\ \mathrm{SO_3}\diagup\\ \mathrm{NO_2}\end{array}\!\!\!\mathrm{Ba} + \mathrm{2H_2O}.$$

This is obtained from the neutral potassium salt by adding barium chloride to a strong solution. The salt forms small granular crystals of a yellowish color, which are difficultly soluble in cold, more easily in boiling water.

.2199 gr. salt gave .0202 gr. H_2O = 9.19 per cent., and .1204 gr. $BaSO_4$ which gives for the dried salt 35.45 per cent. Ba. Theory requires 8.61 per cent. H_2O and 35.86 per cent. Ba.

These results, though not as accurate as could be wished, when taken in connection with the analysis of the acid potassium salt sufficiently indicate the composition of the acid. The barium salt was prepared in small quantity, and was not as pure as was desirable. Another analysis will be made when larger quantities have been prepared.

The proof for the constitution of this acid is as follows: The toluenenitrosulphonic acid, from which it is derived by oxidation, was obtained by Beilstein and Kuhlberg* by the action of fuming sulphuric acid upon orthonitrotoluene (called metanitrotoluene by B. and K., as salicylic acid was at that time supposed to be a meta compound). The same acid was likewise obtained by Engelhardt† by treating his *α*-toluenesulphonic acid with nitric acid. Anna Wolkow‡ has shown that the *α*-acid of Engelhardt is tolueneparasulphonic acid, and she has also made the tolueneorthonitroparasulphonic acid from it by treating it with fuming nitric acid.

Orthoamidoparasulphobenzoic Acid.

Made from the nitro acid by treating the potassium salt with ammonium sulphide. The acid is precipitated from a concentrated solution of its salts on adding hydrochloric acid. It crystallizes in beautiful rhombic plates of a yellowish color, and is tolerably soluble in hot water, slightly in cold water and in alcohol; almost entirely insoluble in ether and chloroform. Dilute solutions of the acid and its barium salt show a beautiful blue fluorescence. An estimation of the sulphur gave the following result:

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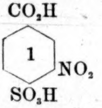
* Liebig's Annalen, 155, 8. † Ibid. 155, 19. ‡ Zeit. f. Chemie, 1870, 324.

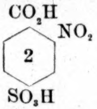
.1951 gr. acid gave .2072 $BaSO_4$ = 14.59 per cent. S. Theory requires 14.70 per cent. S.

The barium salt of this acid has been prepared in small quantity, but no analysis has yet been made. The salt is white, dissolves tolerably easily in hot water, and separates in small crystals which unite to form groups. The salt easily decomposes in solution when evaporated.

In speaking of metamidoparasulphobenzoic acid it was stated that in addition to the proof there given, another consideration led to the same result. This second proof is found in connection with the above orthonitroparasulphobenzoic acid.

According to accepted ideas, but two nitroparasulphobenzoic acids are possible which would have the following formulæ:





Of these, according to the method of its formation, we must accept 2 as the correct formula for the acid last described. This leaves 1 as the only possibility for the other acid, and leads to the same result as the method of proof already given under the latter acid. A comparison of the acid first obtained by Remsen and the one made from orthonitrotoluene, as well as of their salts, given below, shows that they are entirely different.

Metanitroparasulphobenzoic acid contains $2H_2O$ and melts at 130°-131° easily soluble.	*Orthonitroparasulphobenzoic acid* contains no water of crystallization.
Potassium salt; small hard prisms, easily soluble in water.	Potassium salt; very soluble in water.

Acid potassium salt contains $1\frac{1}{2}H_2O$.	Acid potassium salt is anhydrous.
Barium salt contains $4H_2O$. Tolerably soluble. Loses $3H_2O$ over H_2SO_4.	Barium salt is anhydrous. Very slightly soluble.
Amido-acid; white powder, very insoluble, no fluorescence.	Amido-acid; rhombic crystals, quite soluble, strong fluorescence.
Barium salt contains $3H_2O$.	Barium salt contains no water.

The work so far done may be summed up in the statement that two new nitrosulphobenzoic acids have been made, and their structure, as well as that of Remsen's acid, determined. The corresponding amido acids have also been prepared and so far examined that there will be no difficulty in recognizing them, should they again be met with. The acid of Limpricht and Uslar, and the second acid of Griess, have also been prepared in quantity. They are different from any of those examined. As soon as time offers, an attempt will be made to fix the position of the substituting groups. The number of nitro or amido acids now known, which differ from one another, is five. Other possible sources of nitrosulphobenzoic acids are as follows: (1) Action of nitric acid upon orthosulphobenzoic acid.* (2) Of sulphuric acid upon orthonitrobenzoic acid. I have attempted to introduce the sulpho group into metanitro and paranitro benzoic acids in many ways, but entirely without success. (3) Action of sulphuric acid upon ortho and paramido benzoic acids. In the case of paramido benzoic acid the experiment has already been tried by Michael and Norton,† who obtained, not an amidosulphobenzoic acid, but one having the formula $C_{14}H_{12}N_2SO_6$. (4) Action of sulphuric acid upon metanitrotoluene and oxidation of the product. (5) It may be that by treating the two nitro-ethylbenzenes with sulphuric acid, positions will be taken by the sulpho-group different from those in the nitrotoluenes.

After all possible ways have been tried, a thorough study of the salts, ethers, &c., of the isomeric acids will be made. It is proposed to compare 1st, melting points; 2d, solubility; 3d, crystalline form, especially of anhydrous compounds; 4th, number of molecules of water in isomeric salts.

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* Since the above was written an acid which appears to be new has been prepared in this way. The barium salt contains $3H_2O$, which it loses completely over sulphuric acid.

† Ber. der deut. chem. Gesell. 10, 580.

This investigation was undertaken at the instigation of Professor Remsen, and most of the work was done in his laboratory.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(*Continued from page* 284.)

HEAVY CHEMICAL MANUFACTURES—*Continued.*

Salts.

Nitre.—An important addition to our knowledge on the much examined but still obscure subject of nitrification has been lately made by the researches of Mueller, Schloesing, Muentz, Warington and Storer, in reference to the influence of a living ferment in producing this peculiar form of chemical change in nitrogenous material. At the same time new observations have been made upon the range of temperature within which nitrification takes place, upon the unfavorable influence of light, the importance of the presence of calcium carbonate or equivalent basic material, the circumstances under which a nitrite rather than a nitrate is produced, &c. These observations and experimental results will undoubtedly admit of useful application whenever the manufacture of nitre in the so-called "beds" has to be resorted to. Some of the facts recorded by Warington in regard to the influence of light and temperature are quite in accord with results afforded on a larger scale by nitre beds established in the Southern States during the war of 1861–5. The manufacture of ordinary nitre from Chilian sodium nitrate, begun in Germany on a larger scale for the supply of Russia during the Crimean War, has become an established industry, the saline residue from the vinasse of beet-root molasses distillation and the potassium chloride from Stassfurt carnallite being in turn used as the source of the potassium — the latter much the more extensively at present. To no small extent has this process permitted the purchase of Indian saltpetre to be dispensed with, practically removing it from the market of several countries of Continental Europe.

Potassium chloride.—One of the greatest of new industries based upon saline products is certainly the manufacture of this compound from the great beds of carnallite, crude sylvine, &c., overlying the rock salt of Stassfurt and Kalucz. The process is essentially the simple repetition of crystallizations from solutions in which the double salts of magnesium and potassium are broken up, but in its details the method involves nice attention to the varying character of the crude saline mass treated, to the strength of the solutions at various stages, to the temperature, and to the time permitted for crystallization. In the regulation of temperature, steam-jackets to the pans and coils of steam pipe furnish most useful aid, as they do in a host of other processes of modern chemical industry. Much judgment has, moreover, been shown in determining the extent to which the process of purification may be profitably carried in order to supply the different demands of chemical manufactures and of agriculture.

Potassium sulphate.— This salt is also obtained from the material furnished by the Stassfurt beds, and on a much larger scale than was practicable before the discovery of these valuable sources of supply. It has been made by the action of sulphuric acid upon potassium chloride, in decomposing pans like those used in the first stage of the Leblanc soda process, and turning out a product analogous to the common "salt cake," but to a much larger extent from the potassium chloride of carnallite by double decomposition with the magnesium sulphate occurring in adjoining beds as kieserite, or obtainable by the action of water on kainite from other portions of the same remarkable series of deposits.

It is not yet twenty years since these potassium salts were but sparingly obtained by-products from the evaporation of sea-water and from kelp-working. They now represent of themselves important branches of industry, and have served to give new vigor to all manufactures in which potassium compounds are necessary materials.

Potassium chlorate.—The production of this salt has acquired increased importance from its fast extending use in calico-printing and in medicine, as well as in pyrotechny and the making of some kinds of friction matches. The older method of producing it, by passing chlorine into a hot solution of potassium carbonate, has become quite obsolete, and is replaced by the action of chlorine upon milk of lime, followed by conversion of calcium chlorate into the corresponding potassium salt by means of potassium chloride, thus avoiding the measurable waste of potassium by conversion of a dearer into a cheaper salt (carbonate into chloride) to the extent of five-sixths of the whole amount used, and rendering the process at the same time more manageable and well defined. It is interesting to observe that the use of lime was first suggested (though not quite in the way afterwards proposed by Liebig and now practiced) by Graham, whose name we are much more accustomed to associate with researches in pure chemistry and physics than with technical improvements, though for the importance of the latter he seems ever to have had a lively interest.

Potassium pyro-chromate.— For this there is also increased demand owing to extended and varied use, chiefly in dyeing (logwood black, &c.), preparation of pigments for painters' use, and for pigment printing (with chrome yellow, vert Guignet, &c.), and as an oxidizing agent. New sources of supply of the raw material for its manufacture, chromite, have been opened in various directions, including localities in Australia, New Zealand and New Caledonia. The chromite of western North Carolina does not seem to be yet worked, probably on account of defective means of transportation. The use of lime in the roasting of the ore, replacing in part, or sometimes altogether, the potash or more expensive nitre formerly used, proves of much advantage by preventing clear fusion of the alkaline material with subsidence of the heavy ore out of reach of atmospheric oxygen, while potassium sulphate affords the means of converting the calcium salt formed into one of potassium.

Potassium ferro-cyanide.— The history of this salt for some years past has been one of declining production for more direct use in developing dyers' and calico-printers' colors, Prussian blue having been in large measure replaced by the coal-tar colors and ultramarine; but, on the other hand, of increased consumption in making potassium cyanide for the purposes of the electro-plater and photographer. The immense loss of nitrogen, at least 75 per cent. of that contained in the animal matter used, and no small loss of potash, leave this manufacture in the list of those still much needing improvement. The main conditions for diminishing the waste of organic nitrogen being a high temperature, thorough exclusion of air, and rapid heating up of the solid materials introduced into the furnace, it would seem worth trial whether advantage would not be derived from a mechanically regulated feed of very small charges rapidly following each other into a Siemens furnace with non-oxidizing atmosphere. This salt has within the last few years come to be a minor secondary product of the Leblanc process as applied to making potassium carbonate from the Stassfurt chloride. Recent patents for the manufacture of potassium ferro-cyanide from ammonium sulpho-cyanate of gas liquor, or from the same salt made by the action of ammonia on carbon disulphide, seem to be still in the experimental stage only.

Potassium cyanide.— The manufacture of this now largely used compound presents nothing specially new since Liebig's process — fusion together of potassium ferro-cyanide and carbonate — came generally into use, save that soda is often added, and so a mixed product of potassium and sodium cyanides is obtained. No economically successful process has yet been secured for making this or other cyanides from atmospheric nitrogen, in spite of the numerous attempts at producing such a result.

Sodium chloride.—With ever-increasing consumption of common salt, there is little to note of recent important changes in the methods of preparation. In working the mother-liquors from the Mediterranean "salt gardens," the necessity for great storage reservoirs, in which to keep the concentrated solution over until it may be crystallized in the cold weather of winter, has been obviated by the introduction of machinery for the production of artificial cold; but the importance of working these mother-liquors has been much diminished by the products having now to compete with those from the Stassfurt deposits.

Sodium nitrate.— The very simple process of solution and crystallization by which the "Chili saltpetre" of South America is obtained admits of little modification, but the work has been systematized of late years and carried out with improved mechanical arrangements and upon a much larger scale than formerly, so as to provide for the greatly increased demand both for agricultural and manufacturing use.

Sodium sulphate.— The most interesting advance in the manufacture of this salt, so largely in demand for modern glass-making, has been its production by the mutual decomposition of common salt and kieserite (magnesium sulphate), both furnished by the Stassfurt beds. The purity of the product gives it the advantage over ordinary "salt-cake" for the glass manufacture.

Borax.—Greatly increased production is chiefly to be noted, due mainly to the discovery of new sources of supply of the raw material, partly the boro-natro-calcite ("tiza") of South America and the boracite of Stassfurt, but much more the great quantities of crude borax and "tiza" of California and Nevada. Extending use of the salt is observable chiefly in the manufacture of pottery and in connection with washing, but this is hardly in proportion to the greatly increased abundance and lower price.

Ammonium chloride.— The recent proposal of Gerlach deserves attention—namely, to work the "ammonia-soda" process with a view to producing sal-ammoniac, making the sodium carbonate obtained a secondary product only, and not regenerating the ammonia. To this end gas liquor, or that from bone-black works, is to be simply distilled—best in some such apparatus as that of Solvay—the concentrated distillate mixed with brine and treated with carbon dioxide gas under pressure, the precipitated acid carbonate of sodium removed, some ammonium carbonate recovered from the residual solution by distillation, and ammonium chloride then crytallized out, separating it from remaining common salt. A similar process is proposed for making ammonium sulphate and nitrate. It may be worth noticing in relation to these salts, for which the demand is constantly increasing, that enormous waste of ammoniacal liquor prevails, or did but a few years back, at most of the gas works of the United States.

Calcium chloride.—Attention has already been drawn to the great importance of devising a workable process for economically making from this salt and from the corresponding magnesium compound hydrochloric acid or free chlorine. To the list of many other industries which tend to turn out more and more calcium chloride as a waste product may be added salt-boiling in certain regions, as in Ohio, where the mother-liquors are loaded with it.

Calcium acid phosphate.—The immense extension which the trade in "super-phosphate of lime" has taken of late years has led to many small improvements in the mechanical appliances of the manufacture, and some small changes in the chemical treatment used, so as to adapt it to the various phosphatic materials brought into the market, but no change of general importance has been made.

Magnesium sulphate.—The various methods formerly depended upon for the production of this salt have lost interest in view of the immense masses of kieserite found in the upper portion of the Stassfurt beds, this requiring only somewhat prolonged treatment with water to get it into solution, and subsequent crystallization. Although used for a larger number of purposes than heretofore, including sundry applications requiring a cheap soluble sulphate, the price is very low and the available supply in excess of the demand.

Aluminum sulphate.—This salt, though always open to the objection of variability of constitution as it reaches the market, has been made of better quality of late than in former years, more nearly definite in character and freer from iron. Especially is this true of the so-called "porous alum" made from kryolite. Under the name "alum clay cake," that made from clay and still retaining silica in admixture with it finds extensive use among paper-makers and for some of the less refined processes of dyeing, and is manufactured upon an increasing scale, both for such direct use and for conversion into alum.

Alum.—The working of alum shale and alum earth, though still practiced upon a very large scale, has of late years been relatively falling behind, some large establishments having even been abandoned, while clay, beauxite and cryolite have assumed increased importance as sources of the aluminum required, sodium aluminate being first made from the two latter, partly used as such and partly converted into alum. In working shale, moreover, sulphuric acid is largely used now, instead of depending upon the oxidation of the disseminated pyrites.

As regards the alkaline sulphate used in making the double salt, the tendency for a number of years has been towards the substitution of potassium by ammonium sulphate, but this has to some extent been checked, particularly in Germany, by the abundant supplies of potassium compounds from Stassfurt.

Iron (ferrous) and copper sulphates.— Nothing of special importance as to these heavy-metal salts requires notice, except that an extension has been given to the material for their manufacture as secondary products of metallurgic operations, in the growing production of "cementation" copper in the wet way, and in the extraction of gold and silver from copper regulus or copper mattes employed as the means of concentrating the precious metals.

J. W. MALLET.

(To be continued.)

REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

(Continued from p. 291.)

Potassium.— R. Hornberger[*] has shown that the method usually employed for the determination of the alkalies in the ashes of plants is defective, inasmuch as the solution containing these as chlorides — and from which all other constituents of the ashes are supposed to have been removed — still contains phosphoric acid. Hence an error is made in considering as chloride of sodium the difference between the weight of the residue remaining after the evaporation and the amount of chloride of potassium found by means of platinum chloride. The presence of phosphoric acid in this solution is due to the decomposition of phosphate of calcium by carbonate of ammonium, when this reagent, ammonia and oxalate of ammonium are added to the ash solution for the purpose of removing other constituents than the alkalies. It is therefore proposed to precipitate the phosphoric acid as phosphate of calcium by means of ammonia, and remove it by filtration before adding the carbonate and oxalate of ammonium.

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[*] Zeitsch. anal. Ch. 18, 361.

H. Precht[*] announces that the method proposed by A. Carnot[†] for the volumetric estimation of potassium by means of subnitrate of bismuth, hyposulphite of sodium and a standard solution of iodine does not yield satisfactory results.

Lithium.— C. Rammelsberg[‡] has confirmed, by means of new experiments, his former assertion that the precipitate obtained by treating a solution of a lithium salt with phosphate of sodium is in all cases a sodium lithium phosphate; and hence that lithium cannot be correctly determined by the method of Mayer.

Magnesium.— Schlagdenhauffen[§] proposes as a sensitive reagent for magnesium a solution obtained by dissolving iodine in two per cent. caustic potassa or soda until its color becomes golden-yellow. This reagent produces a brownish-red precipitate, or reddish coloration in very dilute solutions of magnesium sulphate or chloride; and the presence of barium, strontium or calcium does not interfere with the detection of magnesium by means of it.

Zinc.—C. Mann[||] determines zinc indirectly by treating the washed sulphide — obtained by conducting sulphide of hydrogen into the acetic acid solution — with moist chloride of silver, and ascertaining by means of Volhard's method the amount of chlorine which passes into solution as chloride of zinc. According to the author the exchange of sulphur for chlorine between zinc and silver takes place rapidly at the boiling temperature of water.

To determine zinc electrolytically, F. Beilstein and L. Jawein[¶] treat the solution of sulphate or nitrate with caustic soda until a precipitate forms, then with cyanide of potassium until a clear solution is obtained, insert the platinum electrode, and connect with a Bunsen's battery consisting of four cells. The zinc precipitates at the rate of about 0.1 gr. per hour.

Cadmium.— To determine cadmium electrolytically, Beilstein and Jawein[**] dissolve the sulphide or oxide in nitric acid, neutralize with caustic potassa, add cyanide of potassium until the precipitate is barely dissolved, dilute so that 75 c. c. of the solution contain only about 0.2 gr. of cadmium, place the beaker in a vessel of cold water, insert the electrode, and connect with a Bunsen's battery of three cells. The average precipitation of cadmium is 0.080–0.090 gr. per hour.

Silver.— Bronner[††] describes how the gas furnace invented by Dr. Hempel[‡‡] may be advantageously employed for the purpose of illustrating the process of cupellation, and even for quantitative assaying.

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[*] Ber. d. chem. Gesell. 12, 1134—from Correspondenzb. des Ver. analyt. Chemiker, 6–10.

[†] Comptes rendus, 83, 390; 84, 1504; 85, 301; 86, 478.

[‡] Jour. Chem. Soc. 1879, 18.

[§] Zeitsch. anal. Ch. 18, 97.

[||] Zeitsch. anal. Ch. 18, 162.

[¶] Ber. d. chem. Gesell. 12, 446.

[**] Ber. d. chem. Gesell. 12, 759.

[††] Zeitsch. anal. Ch. 18, 81.

[‡‡] Zeitsch. anal. Ch. 16, 454.

Mercury.—J. W. Bruehl[*] recommends agitation with a dilute solution of chromic acid as the most effectual method of purifying mercury.[†] L. Meyer[‡] describes a modification of the apparatus formerly proposed by him[§] for the purification of mercury, in which he makes use of ferric chloride instead of nitric acid.[||] G. Attwood[¶]—"Quantitative Assay of the Ores and Compounds of Mercury by the Blowpipe."

Cobalt.—G. Papasogli[**] and T. Tattersall[††] announce that minute quantities of cobalt may be detected by means of the red color developed by yellow sulphide of ammonium in a solution of cobaltocyanide of potassium. The presence of cyanide of nickel or any other soluble cyanides, except that of copper, does not interfere with the reaction. Papasogli and also H. W. Wiley[‡‡] found it possible by means of this test to detect with certainty the presence of 0.0001 gr. of a cobaltous salt when dissolved in 1 c. c. of water.

Iron.—C. Doelter[§§] describes an arrangement of apparatus which may be used with advantage in decomposing silicates with sulphuric and hydrofluoric acids, when it is desired to determine the ferrous iron contained in them by means of permanganate of potassium.

W. F. K. Stock:[||||] "On a new Form of Apparatus for the Production of Ferrous Salts for Titration."

Manganese.—F. Kessler:[¶¶] "On the Determination of Manganese, especially in Iron-Manganese Alloys."

To determine manganese, C. Roessler[***] makes use of the fact that, when a solution containing a manganous salt and nitrate of silver is treated with an alkali, a precipitate is obtained which contains fixed relative quantities of the two metals, namely $Ag_4O.Mn_2O_3$. The solution of manganous salt, which must be free from substances that precipitate silver or reduce the nitrate, is placed in a measuring flask; a measured quantity of a standard solution of silver nitrate, more than is required for the precipitation of the manganese, added; the flask heated upon the water bath, and both manganese and the excess of silver precipitated by means of carbonate of sodium. Ammonia is now added, the flask cooled and filled to the mark, a part of the contents filtered off through a dry paper, and the excess of silver in a measured portion of the filtrate determined by means of Volhard's method. The presence of ferric iron does not interfere with the determination of manganese by this method. The author has found it necessary, however, in the case of solutions of iron-manganese alloys to first remove the iron by means of acetate of sodium, since such solutions, previous to the removal of the iron, contain substances which reduce the nitrate of silver.

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[*] Ber. d. chem. Gesell. 12, 204.

[†] This Journal, 1, 68.

[‡] Ber. d. chem. Gesell. 12, 437.

[§] Zeitsch. anal. Ch. 2, 241.

[||] This Journal, 1. 213.

[¶] Jour. Chem. Soc. 1879, 207.

[**] Ber. d. chem. Gesell. 12, 297—orig. Gazz. Chim. ital.

[††] Chem. News, 39, 66.

[‡‡] This Journal, 1, 211.

[§§] Zeitsch. anal. Ch. 18, 50.

[||||] Chem. News, 39, 46.

[¶¶] Zeitsch. anal. Ch. 18, 1.

[***] Ber. d. chem. Gesell. 12, 925.

J. Pattinson[*] has ascertained that all the manganese in a manganous salt may be precipitated in a state of oxidation equivalent to that of the metal in the superoxide, if the solution containing it and an equal or larger amount of ferric chloride is treated with hypochlorite of calcium or bromine, the temperature raised to 60° or 70°, and an excess of calcium carbonate added. The author utilizes this fact in the determination of manganese in manganiferous iron ores, &c., by an indirect volumetric method.

Chromium.—E. Donath[†] detects chromate of potassium in the presence of bichromate by means of manganese sulphate, bichromate in the presence of chromate by treating with a hot solution of sodium hyposulphite, and free chromic acid in the presence of bichromate by means of potassium iodide.

W. J. Sell[‡] converts chromous compounds into chromic acid by slowly adding to their acidified, boiling solutions a dilute solution of permanganate of potassium until the color of the latter no longer disappears. The conversion is complete; but, since the reduction of the permanganate towards the end of the reaction is only partial, the method cannot be employed to determine chromium volumetrically. To do this the author, after having rendered the solution alkaline with carbonate of sodium, added alcohol and filtered, makes use of the iodine method. To decompose chrome iron ore he recommends fusion, first with potassium hydrofluoride or sodium fluoride and acid sodium sulphate, and then with acid sodium sulphate alone.

Gold.—H. von Jueptner:[§] "On the Separation of Gold and Silver, and on the Determination of the same in Alloys."

Lead.—To determine minute quantities of lead in solution colorimetrically, G. Bischof[||] evaporates to dryness, ignites the residue, digests with the least possible excess of pure hydrochloric acid, filters, washes, conducts sulphide of hydrogen into the filtrate, neutralizes with ammonia, and finally acidifies with hydrochloric acid.

Vanadium.—O. Lindemann[¶] determines vanadic acid volumetrically by titrating in an acid solution with ferrous-ammonium sulphate, which has been strongly acidified with sulphuric acid. The vanadic acid or the corresponding anhydride is reduced to the dioxide. Ferricyanide of potassium, with which a small portion of the solution is from time to time tested, serves to indicate the completion of the reduction. The presence of salts of iron, aluminium, chromium, and the alkalies does not diminish the accuracy of the results.

Hydrocarbons.—W. Hempel[**] finds, that if a mixture of free

[*] Jour. Chem. Soc. 1879, 365.

[†] Zeitsch. anal. Ch. 18, 78.

[‡] Jour. Chem. Soc. 1879, 292.

[§] Zeitsch. anal. Ch. 18, 104.

[||] Zeitsch. anal. Ch. 18, 78.

[¶] Zeitsch. anal. Ch. 18, 99.

[**] Ber. d. chem. Gesell. 12, 1006.

hydrogen, marsh gas and atmospheric air is passed over superficially oxidized palladium under such conditions that the temperature cannot rise above 100°, the hydrogen is completely converted into water, while the marsh gas is wholly unaffected. Mallard and Le Chatelier[*] recommend the use of the hydrogen flame as a means for detecting the presence of fire-damp in mines. The flame becomes distinctly blue when the atmosphere contains 0.25 per cent. of marsh gas; while at least 3 per cent. is necessary to produce the same effect upon the flame of the ordinary miner's lamp, even when a blue glass is used.

R. Angus Smith :[†] "Detection of Fire-Damp."

Hydroxyl Derivatives of Hydrocarbons.—Ch. Bardy and L. Bordet[‡] describe in detail their procedure in determining the methyl alcohol contained in commercial methylenes by Krell's method.[§]

H. R. Proctor[‖]: "Weselsky's Reaction for Phloroglucin."

Organic Acids, Esters and Salts.—To determine acetic acid contained in wine, L. Weigert[¶] places a flask containing a measured amount of it in a water bath filled with a strong solution of common salt, and distils under diminished pressure. Water is added to the residue, and the distillation repeated as often as may be necessary, and the quantity of the acid ascertained by means of a standard solution of alkali. A. Stromeyer[**] states that to ascertain the value of crude commercial acetate of calcium, the acetic acid should be determined, instead of relying on a determination of the calcium as is frequently done; since, by the latter practice, results too high by 4-5 per cent. are obtained.

In order to obtain further confirmation of the presence of so-called ethyldiacetic acid in a urine, which gave the characteristic dark cherry-red color when treated with ferric chloride, A. Hilger[††] mixed 300 c. c. of the urine with 50-60 c. c. of concentrated hydrochloric acid, and distilled off two-thirds of the volume. The residue gave no reaction with ferric chloride. The distillate, however, smelled strongly of acetone, and yielded crystals of iodoform when treated with potassium hydroxide and a solution of iodine in potassium iodide. To further prove the presence of both acetone and ethyl alcohol in the distillate, it was subjected to fractional distillation, and the fractions treated with chromic acid. The portion collected at and under 56° yielded on oxidization formic acid; while that collected after the temperature had risen above 56°, was free from the odor of acetone, yielded the iodoform reaction, and on oxidation, acetic acid and carbon dioxide. To determine approximately the amount of ethyldiacetic acid contained in the urine, 60, 80, or 100 c. c. were mixed with strong hydrochloric acid, and distilled as before; the distillate treated with potassium hydroxide and a strong solution of iodine in iodide of potassium, gently warmed, and allowed to stand in a closed vessel twenty-four hours. The iodoform was then collected in a weighed filter paper, washed with cold water, dried over sulphuric acid and weighed. In this manner, closely agreeing results were obtained from different portions of the same urine.

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[*] Comptes rendus, 88. 749.

[†] Chem. News, 39, 267.

[‡] Bull. de la Soc. Chim. 32, 4.

[§] Ber. d. chem. Gesell. 6, 1030; 7, 1492; 9, 1928.

[‖] Chem. News, 39, 245.

[¶] Zeitsch. anal. Ch. 18, 207.

[**] Ber. d. chem. Gesell. 12, 1135; orig. in Correspondenzb. d. Vereins analyt. Chemiker.

[††] Liebig's Annalen, 195, 314.

B. E. Dietzell and M. G. Kressner:[*] "Investigation of Butter Fat."

J. Koettstorfer[†] proposes, as a new method for detecting the presence of foreign fats in butter, to determine the quantity of caustic potassa required for the complete saponification of a given weight of it. The author found as the result of an examination of thirteen specimens that one gram of unadulterated butter requires for its saponification between 0.2215 and 0.2324 gr. of potassium hydroxide, while the same weight of other fats required in no case more than 0.197 gr.

E. Reichert[‡] has published a method for the analysis of butter which is based on the fact that the proportion of volatile acids in butter is much larger than in other fats. He saponifies a given weight of the material under examination, decomposes the product with sulphuric acid, distils and titrates the acids in the distillate with a standard solution of caustic soda.

According to A. Guyard,[§] a saturated boiling solution of oxalic acid decomposes chlorates, bromates and iodates with liberation of a portion of the chlorine, bromine and iodine, and the reaction may be employed with advantage to detect the presence of these salts. If a solution containing the three is treated with a sufficient quantity of oxalic acid, the chlorate is completely decomposed and the free chlorine driven out by the aqueous vapor and carbon dioxide, while the bromate and iodate remain intact. The addition of more acid, however, immediately induces a decomposition of the bromate. This second stage of the reaction, too, is completed and the free bromine expelled before the third, the decomposition of the iodate, begins.

H. Schiff and S. Pagliani[||] find that the characteristic reaction of salicylic acid with ferric chloride is prevented when 400 parts of sulphuric, 385 of nitric, or 36 of hydrochloric acid are present.

In order to detect salicylic acid in beer and similar dark-colored liquids by means of ferric chloride, Aubry[¶] subjects them to dalysis. Blas,[**] having examined the different

[*] Zeitsch. anal. Ch. 18, 83.

[†] Ibid. 18, 199.

[‡] Ibid. 18, 68.

[§] Bull. de la Soc. Chim. 31, 299.

[||] Ber. d. chem. Gesell. 12, 385.

[¶] Ber. der chem. Gesell, 12, 1135—orig. in Correspondenzb. d. Vereins analyt. Chemiker.

[**] Jour. f. prak. Chemie, 19, 43.

methods recommended for the detection of salicylic acid in beer, concludes that it is simplest and surest to test the urine with ferric chloride a few hours after the consumption of the beer. In this manner the acid may be readily detected when the beer contains only 0.025 gr. to the liter.

Carbohydrates.—F. W. Pavy[*] has published a method for the volumetric determination of glucose which is founded on the fact that a solution of the sugar reduces and decolorizes an ammoniated Fehling's solution without precipitation. The end of the reaction is indicated by the disappearance of the last traces of color from the copper solution. Pavy states that when 100 c. c. of Fehling's solution is mixed with 300 c. c. of ammonia of 0.880 sp. gr. and 600 c. c. of water, one molecule of sugar reduces six atoms of copper from the cupric to the cuprous condition, instead of five, as in the ordinary Fehling's solution. The addition of one gram of potash to 20 c. c. of the solution thus obtained does not alter the ratio of sugar decomposed to copper reduced. If, however, more than one gram and less than five is added, the relation is 1 : 5 — 6; while when five or more grams are added it is 1 : 5, as in the ordinary Fehling's solution. He therefore recommends the use of a solution which is obtained by mixing 120 c. c. of Fehling's solution with 300 c. c. of ammonia of 0.88 sp. gr. and diluting to 1000 c. c. 100 c. c. of this will produce the same reducing effect as 10 c. c. of Fehling's solution.

O. Hehner[†] has examined the method and found it capable of yielding excellent results when the original Fehling's solution contains between 120 and 150 gr. of sodium hydroxide per liter. Between these limits the relation of sugar to copper given by Pavy (1 : 6) holds good, but not otherwise. A controversy has arisen between P. Cazaneuve, D'Arsonval and P. Picard with respect to the merits of Cl. Bernard's method for the determination of glucose in blood.[‡]

E. Salkowski:[§] "On the Compounds of Grape-Sugar with cupric Hydroxide."

J. Riban:[‖] "On the Transformation of Starch into Glucose by Cold Water."

To determine quantitatively the amount of starch in sausage, L. Medicus and E. Schwab[¶] decompose it by means of a diastase solution, treat the products with a little hydrochloric or sulphuric acid, and estimate the grape sugar thus produced by titrating with Fehling's solution.

Nitro Compounds.—F. Hess[**]: "On the Separation of Nitroglycerin from Nitrocellulose."

Alkaloids.—Dragendorff[††]: "On a New Brucine Reaction."

E. Dannenberg[‡‡]: "Detection of Colchicine in Cases of Poisoning."

H. N. **Morse.**

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[*] Chem. News, 39, 77.

[†] Ibid. 39, 197.

[‡] Comptes rendus, 88; 595, 753, 755 and 864.

[§] Zeitsch. anal. Ch. 3. 79.

[‖] Bull. de la Soc. Chim. 31, 10.

[¶] Ber. d. chem. Gesell. 12, 1285.

[**] Zeitsch. anal. Ch. 18, 352.

[††] Zeitsch. anal. Ch. 18, 107.

[‡‡] Zeitsch. anal. Ch. 18, 129.

NOTES.

A Device for the rapid Filtration of the Carbon in Cast Iron and Steel Analyses.

In the analysis of cast iron and steel, much time is consumed in the separation of the carbon by filtration. Even under the most favorable circumstances the operation requires several hours. All attempts at rapid filtration by Bunsen's method, using the usual asbestus filter, proved unsuccessful. The increased pressure either forced the plug of asbestus through the funnel, or if the asbestus was more closely packed, the filtration was rendered exceedingly slow. In order to overcome this defect if possible, a piece of apparatus was constructed, which seems to fulfil all the requirements very successfully.

A piece of platinum foil about .01 mm. in thickness, is cut into a disc, having very near the same diameter as the funnel used, which latter is of the same kind ordinarily used in the estimation of carbon. This disc (Fig. 1.) is perforated with five or six holes, about 1 mm. in diameter, and to its centre at right angles to its plane is soldered, with a minute piece of gold, a stout platinum wire about 1 mm. in diameter, and of such a length that it may extend a short distance below the contracted portion of the funnel (Fig. 2). When the disc is in position, the wire extends down through the smaller portion of the funnel, and tends to keep the platinum plate always horizontal (Fig. 3). Upon this plate is placed a thin layer of pure asbestus. The lower portion of the funnel may be placed through the cork of the receiver of a Bunsen's pump or any other convenient aspirator, as in the usual method of rapid filtration.

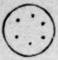

Fig. 1.

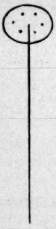

Fig. 2.

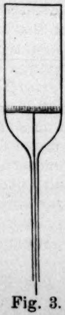

Fig. 3.

The asbestus should be moistened, and the pump set in action before the filtration commences, in order that the asbestus may become well packed before the finely divided precipitate is thrown upon it.

After the operation is finished, and the precipitate well washed, the pump should be allowed to run for a few minutes in order that the precipitate may become comparatively dry. In the state in which the carbon now remains, it may be pushed out of the funnel in a solid coherent cake, by pressure applied to the projecting platinum wire. The tube only requires to be wiped with a small piece of asbestus to render it perfectly clean from the adhering precipitate.

With this apparatus, a filtration which, under ordinary circumstances, would occupy several hours, requires but from twenty minutes to half an hour for its completion.

J. CREAGH SMITH.

UNIVERSITY OF PENNSYLVANIA, *Nov.* 1879.

Potassium Permanganate and the Strychnine Test.

However unsatisfactory they may be, the color reactions of strychnine are still in common use. After dissolving the suspected substance in strong sulphuric acid, it has been customary to add small bits of some oxydizing agent, such as the dichromate or permanganate of potassium, or the dioxides of lead or manganese, and to note the colors which follow.

The permanganate was introduced by W. A. Guy,[*] who claimed for it superiority to the dichromate, and peculiar excellence in respect to brilliancy and delicacy of reaction. As is well known, however, the strong acid present may act upon the salt; slowly, when cold, more quickly when warm, causing evolution of oxygen and vapors of permanganic acid;[†] at the same time more heat is developed, the vapors rise and condense above the liquid in a lustrous film, in which rose-colored drops shortly appear, and finally undergo still further changes of color. Of course the mixture absorbs water with great avidity, and it is asserted by Terreil[‡] that the solution of permanganic acid with sulphuric acid containing three atoms of water is violet in color. Wurtz[§] describes the solution of permanganic acid as of a beautiful red crimson by reflected light, violet by transparent light, and of very great coloring power. It is also known that the solutions of manganic and permanganic salts are colored by many reducing agents,[‖] and it is a fact easily shown, that if readily decomposable organic matter is present, as is often the case in toxical work, the reaction may occur with destructive energy. It will be seen that these reactions, while not necessarily leading to errors, may, nevertheless, under varying conditions, give colors uncomfortably like some of those to be looked for.

Wenzell,[¶] by a long series of experiments, arrived at the opinion that the permanganate gives the most delicate reaction, thus confirming the statement of Guy. His results have been widely quoted, though they have not displaced the use of the dichromate; many still adhering to the latter as altogether superior; others, as Fresenius,* according to the permanganate equal rank.

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[*] Pharm. Journal and Trans. 1861, pp. 558, 602, &c.

[†] Watts, Dict. Chem. 3, p. 819; also, Second Supp., p. 772.

[‡] Quoted by Watts, Dict. Chem. 3, 820.

[§] Dict. Chimie, p. 300.

[‖] Rammelsberg, Leitfaden, &c., 1874, p. 34.

[¶] Am. Jour. Pharm. 1870, p. 385.

I had tested for strychnine the extract from an infusion of *eupatorium*, mentioned in the succeeding note, using dichromate and dioxide of manganese, and had obtained no blue coloration whatever. Using permanganate, however, I secured a most magnificent bluish purple, which was usually developed somewhat slowly, and remained for some time, but at length faded into a dirty reddish brown. Blank experiments showed no such coloration, but if, into one of these a piece of filter paper were let fall, the same blue color soon appeared. Further experiments show that not only filter paper, but bits of woody fibre, tea paper and shreds of cloth give the same reaction, and in one case, very nearly the proper succession of strychnine colors was obtained. The reaction is so delicate that if two dishes are properly cleaned, rinsed with distilled water and dried, one by heat, the other by a clean towel or a sheet of filter paper, the former will give no reaction, the latter a very perceptible blue. Reese† states that the production of a violet color has been noticed in the case of various organic matters by at least one other observer, but does not reject the permanganate on that account. It is not claimed that the succession of colors given by strychnine is ordinarily developed; yet, in view of the possible colors which may arise from the reagents alone, giving nearly every required shade except blue; and in view of the fact that many substances, if present, will afford early in the reaction a very striking blue color; we ought, hereafter, to limit the use of permanganate rigorously to work upon the pure alkaloid. Its employment in toxical cases, where even a minute amount of organic matter may be present, so long as dichromate may be had, is not only unnecessary but dangerous.

W. T. SEDGWICK.

The Relations of Eupatorium and Strychnine.

In a case of suspected poisoning by strychnine which was before the courts not long ago, the affidavit of the chemist employed by the State to make an examination for strychnine reads, according to the newspaper report, as follows: ". . . . The residue obtained from the alcohol in which the stomach was preserved gave, faintly, one of the reactions of strychnine . . . . when dissolved in sulphuric acid and treated with bichromate of potash. As the alkaloid 'curare' produces a similar play of colors, and it is stated that they have been had from organic matter alone, *and I have found them to appear in the extract from an infusion of boneset similarly treated*, it is necessary to insist upon all the other characteristic proofs to identify strychnine. . . ." It should be added that the italics are mine, and that special importance attached to this remark because the deceased had drunk largely of boneset (*eupatorium*) just before his death. Not having met the statement elsewhere, and knowing the very extensive use of the plant as a domestic remedy with no recorded case of lethal effects produced by it, I determined to experiment for myself. Accordingly, in August when the plants were just coming into blossom, I collected a very large supply, dried it in a hot room, pulverized by means of a hay cutter and a drug mill a large amount, using for the purpose the whole plant except the root. Twelve litres of water were brought to 100° in a copper dish and seven hundred grams of the pulverized product put in, the whole kept just below 100° for several hours, and finally filtered hot through cloth and paper. The filtrate was now concentrated over the water-bath and filtered from time to time, the precipitates being preserved. The mass which had been extracted with water was now treated with sulphuric acid, so that the latter was of .2 per cent. strength, and kept warm for some time, the liquid filtered off and also concentrated. An attempt was made to dialyse some of the fluid, in the hope of getting rid of coloring matter and of securing, outside, a sulphate of the alkaloid if any existed. It met with no success.

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* Qualitative Analysis.

† Manual of Toxicology, 1874.

The aqueous extract having become very concentrated, so that it was black, heavy and bitter, an attempt was made to separate from it any strychnine or other alkaloid which might have been present. Some of the liquid was made alkaline with dilute ammonia, ether was added, the whole well shaken and allowed to stand in a separating funnel. Meanwhile some of the same concentrated solution had been carried to dryness over the water-bath, yielding a black, hard and shining extract of very bitter taste. Tests were then made with sulphuric acid and successively dichromate of potassium, dioxide of manganese and permanganate of potassium. Neither the extract from the ether, which was yellowish, amorphous and exceedingly bitter, though scanty, nor the aqueous extract, nor any of the various precipitates obtained by concentration, nor the result of extraction made afterward with ether in acid solution and with chloroform, gave the slightest indication of any reaction similar to that given by strychnine when the dichromate or peroxide was used. The permanganate, however, yielded a beautiful blue passing in some cases into reddish colors, so that but for the discovery described in the preceding paper I should have suspected a reaction similar to strychnine as belonging to *Eupatorium perfoliatum*, L. The extract with sulphuric acid gave results precisely similar, so that I utterly failed to get reactions which would lead to confusion of *eupatorium* with strychnine.

Since making my experiments I learn that Dr. Antisell of the U. S. Patent Office has been led by the obvious importance of the subject to make a similar investigation, and has also completely failed to get any strychnine reaction from either the aqueous or alcoholic extract by using sulphuric acid and dichromate of potassium, with which alone he worked. I have been told that physiological effects have been attributed to *eupatorium* similar to those produced by strychnine. Some experiments which I have lately made upon frogs do not show the least resemblance between them.

W. T. SEDGWICK.

JOHNS HOPKINS UNIVERSITY, *Nov.* 1879.

Latest Developments in the Chlorine Question.

F. SEELHEIM has described an experiment which he has performed, showing that the metal platinum is slowly converted into vapor when heated in a current of chlorine gas. He considers this fact in its bearings upon Victor Meyer's recent experiments on the specific gravity of chlorine at high temperatures, and concludes that Meyer's results are entirely vitiated by it. It will be remembered that Meyer, in his experiments, used platinous chloride, Pt_2Cl_4, and assumed that all the chlorine of this compound is liberated at the temperature employed, while the platinum remains behind.—(*Ber. d. chem. Gesell.* 12, 2066.)

V. MEYER has replied to Seelheim, saying that in his experiments the platinum from the platinous chloride is always found in the form of a solid mass, weighing almost exactly what it should weigh if none of it were converted into vapor. He has further found that the amount of platinum actually converted into vapor when heated in a rapid current of chlorine, is exceedingly small — so small that it could not possibly exert an appreciable influence on the results. More than this, iodine, which is used in the solid form, gives results analogous to those reached in connection with chlorine.—(*Ber. d. chem. Gesell.* 12, 2202.)

Conservatism in Chemistry.

SAINTE-CLAIRE DEVILLE, in commenting on the recent discussions concerning vapor densities in the French Academy, concluded his remarks in the following words: "For more than twenty years past I have endeavored in my teachings and in my writings to combat the intervention of the idea of force in the sciences — of affinity and atomicity in chemistry, for example. I have sought, at least in teaching, to avoid hypotheses which are absolutely gratuitous, like the hypothesis of atoms, of molecules and of hypothetical states of matter, abstractions which always end by being incorporated. I am convinced that all which cannot be demonstrated ought to be rejected, that all which is useless in science is injurious, and I am of the opinion, with my learned friend M. Berthelot, that chemists are following a dangerous road which has been resolutely avoided for several years by the great minds who have laid the foundation of Thermodynamics, Thermochemistry and modern Physiology.

"Before speaking vaguely of gases and vapors, of their atoms, of their molecules, of their combination and their decomposition, it is necessary to study the analogies of gases with liquids, and even with solids, and to endeavor, not to find their constitution, as is said nowadays somewhat boldly, but to find their functions and what they have in common with the functions of substances which are more completely within the perception of our senses. This shall be the subject of a subsequent communication."*

Action of Ozone on Carbon Monoxide.

A. R. Leeds* has shown that, when carbon monoxide and oxygen are passed together through an improved ozonizing battery constructed by him, carbon dioxide is formed; while, if free ozone be brought together with carbon monoxide outside of the ozonizing battery, no union takes place. The latter result confirms that reached some years since by Remsen and Southworth. As Leeds worked with more concentrated ozone than has hitherto been used in like experiments, it seems now to be pretty firmly established that ozone cannot transform carbon monoxide into the dioxide, at least at ordinary temperatures. The transformation which takes place in the ozonizing battery is probably due to the unstable condition into which the oxygen is thrown by the conditions there surrounding it. It may be regarded as in the nascent state. This nascent oxygen probably effects two changes: 1st, that of a part of the oxygen into ozone, and, 2d, that of a part of the carbon monoxide into carbon dioxide.

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* We quote this remarkable passage, not because we are in thorough sympathy with the spirit of the speaker, but to call attention to the fact that Virchowism has its representatives in chemistry as well as in biology. If everything "which cannot be demonstrated ought to be rejected," the impulse to original investigation would surely be much weaker than it now is. "Working hypotheses" are the salvation of any science —Ed.

† Journal Am. Chem. Soc. 1, 450.

The Future of Animal Tar.

Not many years ago the substance known as coal-tar was regarded by chemists as well as by laymen in the light of an uninviting and almost hopelessly complex mixture. To-day, as is well known, it is the source of a large group of highly interesting bodies, and forms the basis of many important industries, some of which are still in their infancy. Certain recent developments in connection with animal tar seem to indicate that there is a future in store for this substance as interesting and as important as the present of coal-tar. It is obtained in largest quantity as a secondary product in factories in which bone-black is made by dry distillation of bones and other animal material. By fractional distillation the tar can be divided into several distinct portions, among which are the bases known as pyridine, C_5H_5N, and picoline, C_6H_7N, which are the first two members of an homologous series. Now, through the researches of Dewar,[*] Ramsay,[†] Weidel,[‡] Hofmann,[§] and others, it has been shown that these bases are intimately connected with such alkaloids as quinine, cinchonine, cinchonidine, berberine, piperine and nicotine. All of these alkaloids when oxidized yield acids which are simple derivatives of pyridine or some other member of the series. The chemistry of the alkaloids is then, in all probability, to be discovered through a careful study of the bases of the pyridine series, and this probability has of late led a number of workers to turn their attention to these bases. It can fairly be prophesied that at no distant time our knowledge of the alkaloids will be materially increased through the aid of investigations now in progress.

[*] Zeitschr. f. Chem. 1871, 116.
[†] Phil. mag. 1877, 246; Ber. d. chem. Gesell. 11, 325.
[‡] Ann. d. Chem. 165, 328; 173, 176; Ber. d. chem. Gesell. 12, 1989.
[§] Ber. d. chem. Gesell. 12, 984.

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